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New Coordination Compounds of Uranium(v).

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NEW COORDINATION COMPOUNDS OF URANIUM(V)

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TO MY MOTHER

AND

IN MEMORY OF MY FATHER

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LIST OF ABBREVIATIONS

diphos . . . . . .ethylenebis(diphenylphosphine)

dipy . . . . . .2,2'-dipyridyl

DTA. . . . . .differential thermal analysis

ESR. . . . . .electron spin resonance

HT . . . . . .tropolone

Ph . . . . . .phenyl

T^- . . . . . .tropolone anion

TCAC . . . . . .trichloroacrylyl chloride

TGA. . . . . .thermogravimetric analysis

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ABSTRACT

Uranium(V), the least stable oxidation state of uranium, forms compounds which are easily oxidized to compounds of uranium(VI) and which readily undergo disproportionation forming stable uranium(VI) and uranium(IV) compounds. The compounds of this unstable oxidation state are very difficult to prepare and study, and as a result uranium(V) chemistry has not been extensively investigated.

This $5f^1$ system is of special interest for spectral studies since it exhibits no electron-electron repulsions and therefore one of the major factors contributing to the complexity of 5f electronic spectra is not present.

Previous work with uranium(V) has resulted in preparation of a considerable number of oxides and alkoxides. The oxides have been rather well characterized but the alkoxides have not been well characterized. Only a few examples of halide addition compounds have been reported and only F^-, Cl^- and O^{2-}, nitrogen and oxygen donor ligands have been complexed to uranium(V) in previous work. In order to gain more information about this unstable oxidation state this work was directed to the preparation and study of new uranium(V) compounds. The study has resulted in the preparation of the first uranium(V) compounds containing U-P, U-As and U-Bi bonds.

It has been found in this study that the reaction

$$UCl_5 \cdot TCAC + xL \rightarrow UCl_5 \cdot xL + TCAC^a$$

can be carried out in benzene solution with a variety of ligands

to produce compounds, $UCl_5 \cdot xL$. Compounds of this type which have been prepared are $UCl_5 \cdot Ph_3P$, $UCl_5 \cdot$ diphos,[b] $UCl_5 \cdot 2C_9H_7NO$[c] and $UCl_5 \cdot 4C_9H_7NO$. A different type of reaction occurs with tropolone, $C_7H_5O_2^- = T^-$, as the ligand in reaction with a solution of $UCl_5 \cdot$ TCAC. In this case TCAC and one chlorine are replaced and the resulting compound is $UCl_4T \cdot 4HT$. Reactions of other ligands with $UCl_5 \cdot$ TCAC have produced the following ionic compounds: $[UCl_4 dipy^d]Cl$, $[U_2Cl_9(Ph_3As)]Cl$ and $[U_2Cl_9(Ph_3Bi)]Cl$. Impure products were obtained with Ph_3Sb, Ph_2SO and other phosphines and arsines.

The new compounds, with one exception, are extremely unstable to moisture and oxygen and preparation of the compounds and subsequent studies were done under an argon atmosphere and in anhydrous, oxygen-free solvents. $UCl_4T \cdot 4HT$ is unique among uranium(V) compounds in that it is stable in dry air for several days. The compounds have been characterized by elemental analyses, conductance measurements, magnetic susceptibility measurements and mass spectra. The uranium(V) oxidation state has been confirmed in the compounds by electron spin resonance, magnetic susceptibility measurements and the electronic spectra.

The g_{ave} ESR values for all the compounds except $UCl_4 \cdot 4HT$ and $UCl_5 \cdot 4C_9H_7NO$ are very close to the value for the free electron. The ESR spectra of all the compounds except $UCl_5 \cdot 4C_9H_7NO$ and $UCl_4T \cdot 4HT$ show a very narrow signal width. These data suggest that the 5f electron of the uranium is strongly delocalized into the

low energy molecular orbitals of the aromatic ring systems in the ligands.

Infrared absorption studies of the CsI region have made possible the assignment of U-N, U-P and U-Cl frequencies. The U-N stretching frequency in $[UCl_4dipy]Cl$ has been assigned as 492 cm^{-1} and in $UCl_5 \cdot 4C_9H_7NO$ as 507 cm^{-1}. The U-P frequency has been assigned as 265 cm^{-1} and 273 cm^{-1} in $UCl_5 \cdot Ph_3P$ and $UCl_5 \cdot$ diphos, respectively. In agreement with previous assignments the U-Cl frequencies are assigned at 325 cm^{-1} and 318 cm^{-1} in $UCl_5 \cdot Ph_3P$, at 330 cm^{-1} and 318 cm^{-1} in $UCl_5 \cdot$ diphos, at 305 cm^{-1} in $[U_2Cl_9(Ph_3As)]Cl$ and at 327 cm^{-1}, 315 cm^{-1} and 310 cm^{-1} in $[UCl_4dipy]Cl$. The electronic spectra of these new uranium(V) compounds are quite complex. The four groups of bands corresponding to the four predicted transitions for an octahedral $5f^1$ systems have been assigned for all the new compounds.

a TCAC = trichloroacrylyl chloride
b diphos = ethylene<u>bis</u>diphenylphosphine
c C_9H_7NO = 8-hydroxyquinoline
d dipy = 2,2'-dipyridyl

HISTORY

Uranium and its compounds have been involved in some of the most significant events in the development of science. The discovery of uranium came in 1789. Martin Klaproth (1743-1817) was carrying out analytical studies to determine the composition of minerals and to develop a chemical classification of minerals. He dissolved pitchblende in nitric acid and neutralized the solution with potash and obtained a yellow oxide. He heated an oil paste of the yellow oxide in a charcoal crucible and produced a black powder with a metallic luster. He concluded that this black powder was a new element which he named in honor of the recently discovered planet Uranus. (1) Klaproth was an important chemist of his time and his analytical studies provided a pattern for analytical chemists who followed him. The following quotation indicates something of the importance of his work. "His conscientiousness further showed itself in the way in which contrary to the custom prevalent among chemists at that day, he published the results of his analysis; instead of merely stating the conclusions presumably arrived at from his experiments, he gave the actual figures of these, and so made it possible to subject them to a minute criticism or correction". (2)

In 1841 Eugéne-Melchior Péligot showed that the black powder obtained by Klaproth was not elemental uranium but uranous oxide, UO_2. (1) Péligot reduced anhydrous UCl_4 with potassium and

isolated a black powder with properties quite different from the oxide obtained by Klaproth. The fact that uranous oxide could not be reduced with carbon or hydrogen probably was an important factor in delaying recognition of the fact that the black powder isolated by Klaproth was not elemental uranium.

In the periodic table which Mendeleéf proposed in 1872 uranium was the heaviest element listed. It remained the heaviest known element until 1940 and the discovery of the first of the transuranium elements.

A series of important discoveries that had great impact on the course of science, especially chemistry and physics, came in the 1890's and early 1900's. Radioactivity was one of the important discoveries of this period. It was first noted by Henri Becquerel in 1896 during his observations of a uranium ore.

In 1938 came another milestone in scientific development. Otto Hahn and Fritz Strassman discovered that uranium atoms could undergo fission as a result of bombardment by slow neutrons. The role of uranium in the field of nuclear energy has elevated it to one of the most important elements. The nuclide ^{235}U is the only naturally occurring nuclide to undergo fission as a result of bombardment by slow neutrons. ^{238}U is used to prepare the synthetic element, plutonium. Neutron absorption by ^{238}U is followed by two successive beta-decay steps to produce ^{239}Pu. ^{235}U and ^{239}Pu are important fuels for nuclear energy.

Uranium is frequently considered as one of the rarer elements; however, it is widely distributed in nature. It has been estimated that the average uranium content in the earth's crust is about 4×10^{-6} gram in 1 gram of rock. (3) This amount ranks the natural abundance of uranium above such common elements as mercury, silver and iodine, but only two minerals, pitchblende and carnotite, are of economic importance, and only limited deposits of these are available. Prior to the discovery of nuclear fission the uranium ores were used as coloring agents for glass and ceramics, but much of the uranium was discarded.

CHAPTER I

INTRODUCTION

A. General Introduction

Uranium compounds are known in which the oxidation state of the uranium is VI, V, IV and III. The relative stability of the oxidation states is VI > IV > III > V. As indicated in the brief history of the element, uranium occupies a singular position among the elements and, as would be expected, its chemistry has been extensively investigated. Previous studies of uranium in this laboratory had been mainly concerned with the coordination chemistry of uranium(IV). The compounds of uranium(V) exhibit a strong tendency to disproportionate to the more stable (VI)and (IV) oxidation states and uranium(V) compounds are easily oxidized to uranium(VI) compounds. Because of the extreme instability of uranium(V) this oxidation state has received much less attention that the more stable oxidation states. To gain more information about this unstable oxidation state an extensive investigation of uranium(V) compounds was undertaken, and the results are described in this dissertation.

The least stable oxidation state, uranium(V) has a ground state electronic configuration of $[Rn]5f^1$. This f^1 system is of special interest for spectral studies since it exhibits no electron-electron repulsions, and therefore one of the major factors contributing to the extreme complexity of 5f electronic spectra is not present. This

lone electron species is, of course, paramagnetic and the study of its magnetic properties would be expected to yield interesting information about the structure and bonding of uranium(V) compounds.

B. Literature Survey of Uranium(V) Chemistry

The published chemistry of uranium(V) will be surveyed before the particular goals and results of this research are presented. For convenience the material is considered according to the following outline:

1. The Compounds of Uranium(V)
    a. Alkoxides, halide alkoxides and related compounds
    b. Oxides and related compounds
    c. Halogen compounds and complexes
    d. Addition compounds of the uranium(V) halides
2. Magnetic Susceptibility Studies
3. Electron Paramagnetic Resonance Studies
4. Spectral Studies
    a. Vibrational spectra
    b. Electronic spectra

1. The Compounds of Uranium(V)

a. Alkoxides, halide alkoxides and related compounds

A considerable number of alkoxides and related compounds have been prepared. Uranium pentaethoxide, a brown mobile liquid,

has been studied by several workers and has been prepared by the following variety of reactions:

$$NaOEt + UCl_4 \rightarrow \overset{O_2}{\underset{heat}{\rightarrow}} U(OEt)_5 \quad (1)$$

$$NaOEt + UCl_4 \rightarrow \underset{heat}{\rightarrow} U(OEt)_5 \quad (2)$$

In reaction (2) the NaOEt and UCl_4 are treated first with Br_2 in benzene solution and then with Na in EtOH to produce $U(OEt)_5$.

$$UCl_5 + Na(\text{in EtOH}) \rightarrow U(OEt)_5 \quad (3)$$

$$UCl_4 + Et_2O + NH_3 \xrightarrow{EtOH} U(OEt)_5 \quad (4) \quad (4)$$

$$U(OEt)_4(\text{in } C_6H_6) + NaOEt(\text{in EtOH}) \rightarrow U(OEt)_5 \quad (5) \quad (5)$$

$$(C_5H_6N)_2UOCl_5 + 5NH_3 + 3EtOH \rightarrow OU(OEt)_3$$

$$OU(OEt)_3 + 2C_5H_5N + 5NH_4Cl \rightarrow U(OEt)_5 + U_{n-1}O(OEt)_{3n-5} \quad (6)$$

(6)

Some physical properties of $U(OC_2H_5)_5$ have been investigated and are reported by Taylor and co-workers. (7)

$U(OMe)_5$ has been prepared by reaction (1), $U(OC_2HCHMe_2)_5$ and $U(OCH_2CF_3)_5$ have been prepared by reaction (4) and $U(OPr)_5$ has been prepared by reaction (2) using the appropriate alcohol as a reactant. (8) Reaction (6) has been used to prepare $U(OPr^i)_5$. (6)

Uranium pentaethoxide has been used as a reactant to prepare a large number of alkoxides and related compounds by an exchange reaction. (7)

$$U(OEt)_5 + 5ROH(\text{ or } xL) \rightarrow U(OR)_5 \text{ (or } U(OR_{5-x}L_x)_5) \qquad (7)$$

Alkoxides, $U(OR)_5$, which R = Me, Pr, Bu, Am, were prepared by the exchange reaction. (9) This work was continued to prepare additional alkoxides in which R = $OCH_2CH_2Pr^i$, $OCH_2CHMeEt$, OCH_2Bu^t, $OCHEt_2$, OCHMePr, $OCHMePr^i$, $OCMe_2Et$, $OCMe_2Pr^i$, $OCMeEt_2$, $OCMeEtPr^i$, $OCEt_3$ and to prepare the mixed alkoxides $U_2(OEt)_5(OBu^t)_5$, $U_2(OEt)_4(OBu^t)_6$, $U(OEt)(OBu^t)_4$. (10) Other compounds prepared by the exchange reaction with $U(OEt)_5$ include $(EtO)_xU(L)_{5-x}$ with x = 2,3 and 4, L = methyl acetoacetate or ethyl acetoacetate (11) and $(EtO)_{5-x}UL_x$ with x = 1, 2 and 3, L = acetylacetone or benzoylacetone. (12)

The exchange reaction with the pentaalkoxides has been used to produce uranium(V) halide alkoxides.

$$U(OR)_5 + nMeOCl \rightarrow U(OR)_{5-n}Cl_n + nMeCO_2R \qquad (8)$$

This reaction has been carried out with R = Et and Pr^i, n = 1,2 and 3 and R = Am^t, n = 1. (13) The analagous reaction has been carried out to form bromide derivatives, $U(OR)_{5-n}Br_n$, with R = Et and Am, n = 1, 2 and 3. (14)

Organosiloxy derivatives of the alkoxides have also been prepared by the exchange reaction.

$$U(OEt)_5 + 5R_3SiOH \rightarrow U(OSiR_3)_5 + 5EtOH \qquad (9)$$

In the above reaction R is Me, Et, $MeEt_2$ or Me_2Et. An alternate method of preparation involved the reaction of the appropriate

silanol in hexamethyldisiloxane with uranium-pentakistrimethylsilyloxide. (15)

$$U(OSiMe_3)_5 + 5R_3SiOH \rightarrow U(OSiR_3)_5 + 5Me_3SiOH \quad (10)$$

The exchange reaction was found to produce $U(OC_2H_5)_3(CF_3COCHCO_2C_3H_5)_2$ when $U(OEt)_5$ was reacted with 2 moles of ethyl 2,2,2-trifluoroacetoacetate. (16)

The acidic behavior of uranium(V) ethoxide was shown through the formation of complexes with more basic alkoxides. The series of compounds $MU(OC_2H_5)_{x+5}$, M = Na, x = 1, M = Ca, x = 2, M = Al, x = 3, was prepared by reaction of uranium(V) ethoxide in absolute ether with the appropriate metal ethoxide.(16) The acidic nature of the $U(OR)_5$ compounds was further illustrated by their ability to form addition compounds with amines. Reactions of uranium(V) alkoxides with acidic reagents brought about cleavage of one or more OR groups. Reactions with one, two or three moles of hydrogen chloride produced $U(OC_2H_5)_4Cl$, $U(OC_2H_5)_3Cl_2$ and $U(OC_2H_5)_2Cl_3$. Addition compounds of the type $U(OCH_2CF_3)_5 \cdot 2(CH_3)_3N$ were formed when penta(2,2,2-trifluoroethoxy)uranium(V) was reacted with various amines.

Some other adducts have been obtained with the alkoxides. The reaction of $U(OEt)_5$ with an excess of Bu^tOH in boiling benzene produced $U(OBu^t)_5 \cdot Bu^tOH$. When this adduct was reacted with pyridine a new adduct, $U(OBu^t)_5 \cdot C_5H_5N$ was formed. (10) Adducts were also

reported with halide alkoxides, $U(OR)Cl_4 \cdot MeCO_2R$ (R = Et and Pr^i) (13) and $U(OR)Br_4 \cdot CH_3COR$ (R = Et or Am). (14)

Other alkoxides which have been prepared include $U(OCH_2CH{:}CH_2)_5$, $U(OCH_2CH_2NEt_2)_5$ and $U(OCH_2CH_2SCH_2CF_3)_5$. (8)

The proton magnetic resonance spectrum of $[U(OEt)_5]_2$ has been studied in $CFCl_3$ and $CDCl_3$. (17) These studies indicate that from -65°C to room temperature the structure of the dimer involves a double alkoxide bridge and 6-coordinated U(V) ions. The spectrum obtained at the lower temperature indicates an increase in molecular complexity. The spectrum of $U(OPr^i)_5$ suggests a mixture of monomer and dimer at room temperature with predominately the dimer form at low temperature.

Only a few studies have been done with this class of compounds. The few physical properties which have been reported for the foregoing compounds are tabulated in the recent review of uranium(V) chemistry. (18)

b. Oxides and related compounds

In the course of a study of uranium oxides (19) reported in 1948 the first perparation of U_2O_5 is described. U_2O_5 was prepared by heating the calculated amounts of UO_2 and U_3O_8 or UO_3 to about 1100° C in sealed evacuated quartz capillaries. Single crystals of U_2O_5 were prepared during this study by thermal decomposition of UO_2Cl_2 at 900°C. The unit cell of U_2O_5 is orthorhombic, a = 8.27±0.02Å,

b = 31.65 ± 0.1Å, c = 6.72 ± 0.02Å, and there are 16 U_2O_5 per unit cell. From UO_3 to U_2O_5 a one phase region exists in which the various structures continuously change from one to another.

The reaction of UO_3 with H_2SO_4 at 80°C yields U_2O_5 and the reaction of U_3O_8 and H_2SO_4 yields U_2O_5 in the temperature range 0 - 140°C. (20)

The composition, structure, thermal resistance and conditions for synthesis of U_2O_5 have been investigated by other workers. (21) U_3O_8 may be dissovled in 10-15% H_2SO_4 to produce U_2O_5. Following a dissolution period of 2.5 - 3 hours, the U_2O_5 is obtained. U_2O_5 is stable below 200°C. X-ray phase analysis shows an irreversible phase transformation which occurs in the range 200° - 300°C to produce $U_5O_{13\pm x}$ and oxidation of U_2O_5 to U_3O_8 occurs in the range 300° - 400°C. It is stated above that U_2O_5 is orthorhombic, however, this more recent study (21) reports a hexagonal structure. It is pointed out that the structure of U_2O_5 is quite different from that of rhombic U_3O_8 and U_5O_{13} but that it is much closer to the structure of hexagonal U_3O_8 and α - U_3O_8.

The existance of U(V) ions is assumed in UO_{2+x} to account for defect ordering and its variation with temperature. The notable defects are considered to be O ions in stable association with O vacancies and U(V) ions and unassociated U(V) ions.(22)

Many uranates and diuranates of U(V) have been prepared. Heating UO_2 with Li_2UO_4 or Na_2UO_4 <u>in vacuo</u> at 650° - 750°C gives

$LiUO_3$ and $NaUO_3$. (23) It is reported that the resistance of these compounds to water and acids exceeds that of their U(VI) counterparts. $CrUO_4$ is found to be present in a study of the system Cr_2O_3-UO_2-O_2. (24) $BiUO_4$ is formed by the following reaction:

$$2Bi_2O_3 + U_3O_8 + UO_2 \rightarrow 4BiUO_4 \qquad (11)$$

The magnetic behavior and the absorption spectrum in the near infrared region confirm the U(V) oxidation state. $BiUO_4$ crystallizes in the fluorite structure. (25).

The first of a series of papers on ternary oxides of U(V) describes the preparation of a number of U(V) oxides. The preparation, properties and lattice constants are given for MUO_3 (M = Li, Na, K, Rb), $M'U_2O_6$ (M' = Co, Ni, Mg, Mn, Cd), $0.15Li_2O \cdot U_2O_5$, $0.5Li_2O \cdot U_2O_5$, $Na_2O \cdot U_2O_5$ and $K_2O \cdot U_2O_5$. (26) A study of the ternary oxides of U(V) with trivalent cations (27) continues this series. A fluorite structure is found for MUO_4 (M = Sc, Y, Nd, Sm, Eu, Gd, Yb and Bi). $FeUO_4$ and $CrUO_4$ are found to be isomorphous and the reflectance spectra of $CrUO_4$ is considered to confirm a coordination number of six in the compound.

MgU_2O_6 and CaU_2O_6 have been prepared by thermal decomposition of MU_2O_7. BaU_2O_6 is prepared by reduction of BaU_2O_7 with ammonia at 600°C. (28,29).

$Ba_2U_2O_7$ was prepared by Scholder and Bixner (30) and in a recent study of this compound by Kemmler-Sack (31) the compound

was prepared by the following reaction:

$$Ba_2UO_5 + UO_2 \rightarrow Ba_2U_2O_7 \qquad (12)$$

$Ba_2U_2O_7$ is monoclinic with a deformed pyrochlorstructure.

Mixed metal oxides containing U(V) have been studied. The first report (32) of such compounds states that the composition is assumed from cation ratios in the mixtures and gives no additional confirmation of the pentavalent state of uranium. The compounds reported are $BaMUO_6$ (M = Cr, Sc, Y, Er, In) and Sr_2MUO_6 (M = Cr, In). A more detailed study of a compound of this type concerns Ba_2UFeO_6. (33) The compound is formed when the following reactions occur in a heated quartz ampule sealed under vacuum.

$$Ba_3UFe_2O_9 + BaUO_3 \rightarrow 2Ba_2UFeO_6 \qquad (13)$$

$$Ba_2FeO_4 + UO_2 \rightarrow Ba_2UFeO_6 \qquad (14)$$

$$Ba_3UO_6 + BaUO_4 + 2/3(Fe_2O_3 + Fe) \rightarrow 2Ba_2UFeO_6 \qquad (15)$$

The presence of U(V) is confirmed from a study of the paramagnetism. A crystallographic study of the mixed oxide shows it is a perovskite and the probable space group is Fm3m.

Oxohalide compounds have been prepared containing the UO_2^+ and UO^{3+} ions. Prigent has prepared and studied $UOBr_3$. (34,35,36) The compound is prepared by reaction of carbon tetrabromide on UO_3

above 110°C.

$$2UO_3 + 4CBr_4 \rightarrow 2UOBr_3 + 4COBr_2 + Br_2 \qquad (16)$$

The oxobromide begins to decompose at 200°C and is completely dissociated to $UOBr_2$ and Br_2 at 300°C. The dismutation of $UOBr_3$ in aqueous solution has been studied as a function of concentration and pH. (37) The study of the dismutation of $UOBr_3$ was extended to non-aqueous solvents, (38) and it was observed that in solvents which do not contain oxygen that the rate of dismutation is slow compared to that in water.

$UOCl_3$ has apparently been prepared by the reaction of UCl_4 with UO_2Cl_2, (39) and it has been reported as an intermediate in the preparation of a higher uranium chloride by the reaction of CCl_4 on UO_3. (40) An exchange reaction between $MoCl_5$ and UO_3 has recently been reported to yeild $UOCl_3$. (41)

$$UO_3 + MoCl_5 \rightarrow UOCL_3 + MoO_2Cl_2 \qquad (17)$$

The reaction occurs in an evacuated glass ampoule at 200° - 300°C. The hydrolysis products of $UOCl_3$ were investigated by infrared absorption studies, (42) but there is little information available on $UOCl_3$ <u>per se</u>.

The first compound containing the UO_2^+ which was isolated in the solid state is UO_2Br. (43) The preparation involves the reaction of UO_3 with HBr at 250°C.

$$UO_3 + 2HBr \rightarrow UO_2Br + 1/2Br_2 + H_2O \qquad (18)$$

The product is a brown solid, which is stable to 500°C. If the reaction is carried out at ambient temperature a hydrate, $UO_2Br \cdot 2H_2O$ is obtained while at -20°C the product is $UO_2Br_2 \cdot H_2O$, a U(VI) compound. Levet (44) has very recently reported the preparation of UO_2Cl by reduction of UO_2Cl_2 with UO_2 at 590°C or at the same temperature by the reaction of U_3O_8 and UCl_4. The latter reaction is carried out under argon for 72 hours. The brown-violet needles of UO_2Cl are stable under argon up to 600°C. X-ray diffraction studies are reported for this compound and magnetic data is presented to confirm the oxidation state.

A study of uraniumoxofluoride phases, UO_xF_y (x = 2.00 - 2.58, y = 0.17 - 1.00) includes 5 phases containing pentavalent uranium: $UO_{2.33}F_{0.33}$, $UO_{2.25}F_{0.50}$, $UO_{2.17}F_{0.67}$, $UO_{2.08}F_{0.83}$, $UO_{2.00}F_{1.00}$. Magnetic susceptibility and spectral data are reported to support the structures given. The compounds have strong structural relationships to the oxides U_2O_5 to UO_3 and contain O-U-O chains. (45)

Recent magnetic and spectroscopic studies have confirmed the presence of UO_2^+ in the series of compounds $KPbU_2O_6F$, $RbPbU_2O_6F$ and $TlPbU_2O_6F$. (52) Crystal constants are also given for these compounds. It is found that $Pb_2U_2O_7$ forms solid solutions with $NaUO_3F$ up to the composition $Pb_2U_2O_7 \cdot NaUO_3F$. (46) The preparation of pyrochloro-type compounds $A'AU_2O_6F$ (A' = Na, K, Rb, Tl and A = Sr, Pb, Ba), space

group O_h^7-Fd3m, is reported. (46) The compounds are prepared by the following three methods:

$$2A'F + 2AUO_4 + 2UO_2 \rightarrow 2A'AU_2O_6F \quad (19)$$

$$AF_2 + A'_2UO_4 + AUO_4 + 2UO_2 \rightarrow 2A'AU_2O_6F \quad (20)$$

$$A'_2UO_4 + 2AO + UO_3 + 1.5UO_2 + 0.5UF_4 \rightarrow 2A'AU_2O_6F \quad (21)$$

Magnetic and spectral studies of the compounds (47) show that $KSrU_2O_6F$, $RbSrU_2O_6F$, $KBaU_2O_6F$ and $RbBaU_2O_6F$ are regular uranium-oxygen octahdra while the other compounds prepared are distored octahedrons.

UO_2^+ is formed when $MgUO_4$ is dissolved in LiCl-$MgCl_2$ at 650°C. UO_2^+ is also formed when UO_2Cl_2, U_3O_8 or UO_3 is dissolved in various molten salt solutions. The presnece of UO_2^+ is identified in these investigations by a study of the spectra over the region 500 to 1900 mμ.(48,49) The spectral data will be discussed in the section on spectral studies.

Treatment of an alcoholic solution of $UCl_5 \cdot SOCl_2$ with pyridine was reported to produce $(C_5H_6N)_2UOCl_5$. (6) However, recent information (50) indicates there may be a question as to whether this compound contains U(V). The authors indicate that their data does not rule out a mixed U(IV) - U(VI) compound.

The compounds R_2UOBr_5 and R_2UOCl_5 (R = Et_4N^+ or Ph_4As^+) have been prepared and studied. The compound $(Et_4N)_2UOCl_5$ is found to be stable in air but not toward high humidity. (50).

An extensive list of references concerning the study of UO_2^+ in solution has been presented in the recent review of uranium(V) chemistry. (18) It is concluded that UO_2^{2+} undergoes reduction to produce UO_2^+ and the reversible nature of the reduction is considered strong evidence for the same degree of oxygenation in the U(V) and U(VI) species.

Calculations show that the well defined periodicity in the changes in equilibrium constant for the disproportionation of MO_2^+ (M = U or other actinide elements) is associated with changes in the parity of the electron configuration of the ions. (51) It is reported that changes in parity affect to a marked extent the potentials of M(V) - M(VI) pairs and to a lesser extent the potentials of M(IV) - M(VI) pairs.

A recent report describes the preparation of the first U(V) sulfide. (52) KUS_3 is prepared by mixing an excess of sulfur with KUS_2 in a vycor tube under argon and heating at 750°C for several days. It was noted that the black crystals of KUS_3 are less oxidizable and less hygroscopic than KUS_2. A study of magnetic susceptibility confirms the pentavalent state of uranium.

c. Halogen compounds and complexes

The pentavalent halides, UF_5, UCl_5 and UBr_5, are known but UI_5 has not been prepared. UF_5 can be prepared by reaction of UCl_6 with anhydrous HF (53) and by heating UF_4 with an excess of UF_6 at

95° - 100°C for 20 - 100 hours. (54) A semi-continuous process for the preparation of UF_5 has been devised using the following reaction: (55)

$$2UF_6 + 2HBr \rightarrow 2UF_5 + 2HF + Br_2 \qquad (22)$$

The melting point of UF_5 is 348°C. (56) The formation of UF_5 is noted as a minor product in the reaction between UF_4 and BrF_5. (57) The crystal structure has been determined for α-UF_5 and β-UF_5. Both modifications are tetragonal body-centered structures. In α-UF_5 each uranium atom is bonded to six fluorine atoms, while in β-UF_5 each uranium atom is bonded to seven fluorine atoms. (58) The transition temperatures of α and β-UF_5 is calculated as 125°C from equations for equilibrium pressure. α-UF_5 is stable above 125°C; however, complete conversion of the β form may require twelve hours at 185°C. (40)

A description of a reaction of UCl_5 with PCl_5 to form $UCl_5 \cdot PCl_5$ which appeared in the year 1873 seems to be the first reference in the literature to a uranium(V) compound. (59) A method of preparation of UCl_5 was given in an article appearing the following year. (60) UCl_5 is formed when a mixture of dry Cl_2 is heated with pure carbon and an oxide or oxychloride of uranium. A slow reaction produces needle-shaped ruby red crystals while a fast reaction produces a brown powder. Heating UO_3 or U_3O_8 in a sealed tube with Cl_2 or

CCl_4 produces UCl_5. (61) The presence of UCl_5 was noted as an intermediate during the reaction of UO_3 and hexachloropropene to prepare UCl_4. (62) The molecular weight determined by ebullioscopy in CCl_4 indicates that UCl_5 occurs as a dimer in solution. (40) A crystal structure determination of UCl_5 shows that it forms monoclinic crystals. (63) The structure has a cubic closest packing of chlorine atoms, in which uranium atoms occupy one-fifth of the octahedral holes and two such octahedra from a dimeric unit. Thus, the existance of UCl_5 as a dimer in the solid state and in solution is confirmed.

UBr_5 has been prepared and studied by Prigent. (35,64,65) The compound is prepared by the reaction of UO_3 and CBr_4 or by the reaction of UO_3 and $COBr_2$. UBr_5 decomposes on heating to produce UBr_4 and Br_2.

Some very interesting results of studies of U(V) in aqueous solution have been reported. Early work on U(V) in aqueous media involved only very dilute solutions (10^{-3}M) of UO_2^+ in the narrow pH range 2 - 4. (66,67) The U(V) ion is rapidly hydrolyzed in aqueous solutions to UO_2^+ which has been found to be very unstable toward disproportionation into U^{4+} and UO_2^{2+}. (3) Rampy prepared NH_4UF_6 by the reaction of gaseous NH_3 on an excess of UF_6. The $NH_4F \cdot UF_5$ is soluble in concentrated aqueous HF. (68) The report of the stability of this compound in aqueous solution led other workers to attempt to prepare uranium(V) fluorides in aqueous solution.

NH_4UF_6 has also been obtained by the reaction of liquid UF_6 on NH_4F at 120°C. (69) The product obtained in this case was reported to be decomposed by water vapor.

Asprey and Penneman (70) found that when UF_6 is dissolved in aqueous HF surprisingly stable solutions of U(V) result. The blue, crystalline compound, $HUF_6 \cdot 2.5H_2O$ is formed by cooling a 5M solution of U(V) to -10°C. The absorption spectrum of this compound has a prominent absorption at 1.36μ which is very similar to that found in the spectra of anhydrous $LiUF_6$, $NaUF_6$ and $CsUF_6$ (vide infra). The lower hydrate $HUF_6 \cdot 1.25H_2O$ is obtained from a solution of U(V) in 85-90% HF.

The direct reaction of UF_5 and NH_4F or the alkali fluorides produced compounds of the type $MF \cdot UF_5$ (M = NH_4, Li, Na, K, Rb and Cs). The compounds exist with the ratios of 1:1, 2:1 (except Li and Na) and 3:1 (except Li) but no cases of $4MF:UF_5$ were found. The compounds were characterized by X-ray powder diffraction. The relationship of structure and spectra are considered in a later section. (71,72) To produce single crystals of MUF_6 (M = Li, Na, K, Rb, Cs and NH_4) finely divided UF_5 has been mixed with the appropriate fluoride and treated with anhydrous liquid HF. (73) The rhombohedral compounds $LiUF_6$, $NaUF_6$ and $CsUF_6$ are a clear blue while the pseudo-hexagonal compounds KUF_6, NH_4UF_6 and $RbUF_6$ are pale yellow-green. A crystal structure determination of $CsUF_6$ has shown the compound to be rhombohedral and in the space group $R\bar{3}$. (74)

The uranium atom has the six fluorine neighbors at 2.057Å which indicates an octahedron slightly compressed along the three fold axis.

A reaction of NO with UF_6 produces an ionic nitrosyl salt. The reaction can be represented by the following equations:

$$NO(g) + UF_6(g) \rightarrow NOF(g) + UF_5(s) \quad (23)$$

$$NOF(g) + UF_5(s) \rightarrow NO^+[UF_6]^-(s) \quad (24)$$

X-ray diffraction data shows that the gross geometrical arrangement involves an NO^+ ion in the center of a cube with UF_6^- ions at the corners. (75)

UF_6 reacts with hydrazinium(+2)fluoride in liquid HF to produce $N_2H_6(UF_6)_2$. When excess hydrazinium fluoride is present $N_2H_6UF_7$ is produced. (76,77) The magnetic susceptibility data and near infrared spectra of the compounds were presented which confirm the presence of U(V) in the compounds.

A series of fluoride complexes have been prepared by the reaction of a divalent metal fluoride with a solution of UF_5 in 40-50% HF. The reaction produces an immediate, abundant precipitate of $MU_2F_{12} \cdot 4H_2O$ (M = Co, Ni, Cu). The compounds were characterized by Debye-Scherrer patterns and infrared spectra and chemical analyses. The near infrared spectra shows the characteristic bands of U(V). (78,79)

Na_3UF was prepared by the reaction of $NaUF_7$ with F_2 in a copper tube at 390° - 400°C. (80) The magnetic moment determined from susceptibility coefficients in the temperature range 77° - 453°C was 2.29 Bohr Magnetons.

The hexachlorouranate(V) compounds could not be prepared in aqueous solution due to the rapid disproportionation of U(V) in HCl. The hexachlorouranate compounds were prepared by reaction of chlorides with a thionyl chloride solution of UCl_5. (81) Magnetic, crystallographic and spectral properties were presented for $MUCl_6$ (M = Cs, Me_4N, Me_2HN, and Ph_4As). The octachlorouranate(V) compound, $(Me_4N)_3UCl_8$, was prepared by the same reaction. A conductometric study of an addition compound of $UCl_5 \cdot SOCl_2$ with pyridine was made. The results indicated the presence of UCl_6^-, UCl_7^{2-}, and UCl_8^{3-} in solution. Other hexachlorouranates(V) have been prepared by a different method. $RbUCl_6$ and $(C_3H_7)_4NUCl_6$ are produced by reaction of the appropriate chloride with $UCl_5 \cdot$ TCAC in thionyl chloride. (82) The spectral data and other data for the compounds is discussed in a later section.

Ryan (50,83) has prepared hexabromouranates(V) and hexaiodouranates(V). UBr_6^- is obtained in dry methane by oxidation of UBr_6^{2-} with Br_2. Salts of Et_4N^+ and Ph_4As^+ have been prepared by this technique. The method can also be used for preparation of hexachlorouranates(V). Salts of UI_6^- are prepared by treating salts of UCl_6^- or $UO_2Cl_4^{2-}$ with anhydrous liquid HI. UI_6^- salts are extremely

unstable and decompose above $-30^{o}C$.

d. Addition compounds of the uranium(V) halides

Only a limited number of U(V) addition compounds have been prepared. The following adducts have been reported for alkoxide compounds of U(V): $U(OBu)_5 \cdot C_5H_5N$, $U(OBu^t)_5 \cdot Bu^tOH$, (10) $U(OR)Br_4 \cdot CH_3COOR$ (R = Et or Am) (14) and $U(OR)Cl_4 \cdot MeCO_2R$ (R = Et or Pr^i). (13) Gas chromatography and infrared spectrum were used to confirm the presence of C_5H_5N in $U(OBu)_5 \cdot C_5H_5N$. Analyses and colors are the only properties given for the other compounds.

Because this dissertation is primarily concerned with the preparation and study of halide addition compounds, the compounds of this type reported prior to the present study will be discussed in more detail than the other classes of compounds. The first reference in the literature of U(V) compounds concerns the preparation of the compound formulated $UCl_5 \cdot PCl_5$. (59) The compound was prepared by reaction of UCl_5 and PCl_5 in a sealed tube. The compound has also been prepared by this reaction: (84)

$$UO_3 + 4PCl_5 \rightarrow UCl_5 \cdot PCl_5 + 3POCl_3 + 1/2Cl_2 \qquad (25)$$

When the compound undergoes electrolysis in $POCl_3$ it is found that UCl_6 is liberated at the anode while PCl_3 and PCl_5 are liberated at the cathode. The authors consider that $UCl_5 \cdot PCl_5$ exists in nonaqueous ionizing solvents as (PCl_4^+) and (UCl_6^-). The compound disproportionates in water yielding tetravalent and hexavalent uranium.

The absorption spectrum was given for the region 300 to 1000 mμ. Sharp maxima occur at 960 mμ and about 875 mμ with very strong absorbance beginning at 540 mμ. (84)

When UO_3 is heated between 150 - 200°C in a sealed tube with thionyl chloride, UCl_5 in the form of an addition compound is produced. $UCl_5 \cdot SOCl_2$ is a red-brown crystalline compound. The reaction of UO_2Cl_2 and $SOCl_2$ also produces the addition compound. (85) The refluxing of UO_3 with thionyl chloride for 14 days was found to be a more suitable procedure than the sealed tube technique for the preparation of larger amounts of $UCl_5 \cdot SOCl_2$. (6) $UCl_5 \cdot SOCl_2$ is believed to exist as $(SOCl^+)(UCl_6^-)$. (86) The adduct $UOCl_3 \cdot 2EtOH$ has been reported to form from the reaction of $UCl_5 \cdot SOCl_2$ and EtOH. (6)

A modification of the procedure for the preparation of UCl_4 by the reaction of UO_3 and hexachloropropene was used by Panzer and Suttle in an attempt to produce UCl_5. (87) However, they obtained a dark red crystalline complex compound which they formulated as $5UCl_5 \cdot CCl_2 = CClCOCl$. A careful study of this compound (82) showed that the product was not $5UCl_5 \cdot CCl_2 = CClCOCl$ but $UCl_5 \cdot CCl_2C = CClCOCl$. This compound, pentachloro(trichloroacrylyl-chloride)uranium(V), has been used in the present study to prepare a variety of new compounds. The details of preparation and properties of $UCl_5 \cdot$ TCAC will be discussed in the section on the preparation of new compounds.

Two other chloro addition compounds have been reported, $UCl_5 \cdot Ph_3PO$ and $UCl_5 \cdot (C_8H_{17})_3PO$. (88) These compounds are obtained when a suspension of $CsUCl_6$ in methylene chloride is treated with the ligand. An intense red solution of the complex is formed along with solid CsCl. After separation from CsCl, the $UCl_5 \cdot Ph_3PO$ is isolated by vacuum evaporation of the solvent or by precipitation with isopentane. $UCl_5 \cdot (C_8H_{17})_3PO$ was isolated by vacuum evaporation. The triphenylphsophineoxide complex is a yellow-orange crystalline solid and that of tri-octylphosphineoxide is an orange-red oil. The complexes are decomposed by moisture, but are quite stable under argon or in anhydrous methylene chloride solution. Reactions similar to those above were obtained with benzyldiphenylphosphineoxide and octyldiphenylphosphineoxide, but information on the isolated products was not given. The red solution was obtained using hexamethylphosphoramide, however, disproportionation occurred within a few minutes.

The first addition compounds of UBr_5 have recently been reported. (89) UBr_5 is obtained by oxidation of UBr_4 by liquid bromine. Subsequent treatment with triphenylphosphineoxide or hexamethylphosphoramide in anhydrous methyl cyanide produced soluble complexes. The dark red complexes were isolated by vacuum evaporation of excess oxidant and solvent.

2. Magnetic Susceptibility Studies

Magnetic susceptibility measurements have been reported for

many of the U(V) oxides and some of the halide and halide addition compounds. Recent reports include the measurements for oxides, an alkoxide and a sulfide compound. The magnetic susceptibility measurement (room temperature) gave the value 530 ± 20 x 10^{-6} cgs units for χ_M for $[U(OC_2H_5)_5]_2$ and this leads to μ_{eff} = 1.12 BM. (17) Magnetic moment determination has confirmed the presence of U(V) in U_2O_5. The magnetic moment is μ_{eff} = 1.47 ± 0.02 BM. (90) Values reported by these same workers for other oxides are μ_{eff} = 1.39 ± 0.02 BM for U_3O_8 and μ_{eff} = 1.62 ± 0.02 BM for U_5O_{13}. It is suggested that these values indicate the presence of 4 and 2 atoms of U(V) per U(VI) atom, respectively, in U_5O_{13} and U_3O_8. Other studies of U_3O_8 have given values of μ_{eff} = 1.64 BM (293°K) (91) and μ_{eff} = 1.63 BM.(92) It is concluded from these studies that U_3O_8 is a 2 to 1 molar ratio combination of U(V) and U(VI). A recent study (93) reports a value of μ_{eff} which gives satisfactory agreement with the values given above. However, when the χ_U^{5+} is calculated for the formula $0.5(U_2O_5 \cdot UO_3)$ considering the temperature dependent paramagnetism of UO_3 and the diamagnetic correction for U^{5+} and O^{2-} the resulting value is μ_{eff} = 1.32 at 295°C. As a result the formula proposed for U_3O_8 is $U_2O_5 \cdot UO_3$.

The magnetic moments of $LiUO_3$ and $NaUO_3$, calculated from susceptibility data over the temperature range 77 - 480°K, are 1.81 BM and 1.66 BM respectively. The compounds obey the Curie-Weiss Law over this temperature range. (94)

The magnetic susceptibility of a number of ternary uranium(V) oxides have been measured. (93) The following values were included:

1. For compounds of the type formula MUO_3 (M = Li, Na, K, Rb) the values of μ_{eff} are between 1.06 and 1.23 BM at 293°K, 293°K, 296°K and 303°K.
2. For compounds of the type MU_2O_6 (M = Mg and Cd) the values of μ_{eff} are 1.50 BM and 1.43 BM at 293°K.
3. For compounds of the type MUO_4 (M = La, Y, Sc, Bi) the values of μ_{eff} are 1.42 BM, 1.56 BM, 1.43 BM and 1.51 BM at 293°K (except for $BiUO_4$ measured at 297°K).
4. For the compound Sr_2InUO_6 the value of μ_{eff} is 0.93 BM. The magnetic data of these uranium(V) oxides are considered to be consistant with a ground state configuration f^1 perturbed by spin-orbit coupling and octahedral ligand fields. Measurements over a ragne of temperatures show that the compounds do not follow the Curie-Weiss Law.

Additional studies on compounds of the type MU_2O_6 have been made. Brochu and Lucas (29) report that CaU_2O_6, BaU_2O_6 and SrU_2O_6 are paramagnetic over the range 85° to 300°K. The results obtained do not exactly follow the Curie-Weiss Law. A correction was made for the presence of a temperature independent paramagnetism and the results then followed the law. The magnetic moments calculated

are as follows; CaU_2O_6, μ_{eff} = 1.79 ± 0.02 BM, SrU_2O_6, μ_{eff} = 1.82 ± 0.02 BM and BaU_2O_6, μ_{eff} = 1.68 ± 0.02 BM.

Leroy and Tridot (90) give a value of μ_{eff} = 1.76 ± 0.02 BM for CaU_2O_7. They also confirm the presence of UO_2^+ in $CaUO_{3.66}$ and $CaUO_{3.5}$, on the basis of the magnetic moments, μ_{eff} = 1.33 ± 0.02 BM and μ_{eff} = 1.83 ± 0.02 BM, respectively.

The mixed oxide Ba_2UFeO_6 is found to be ferromagnetic and the presence of U(V) in the compound is confirmed by the magnetic data. (33)

The magnetic moments for a series of oxyfluorides have been reported by Kemmler-Sack. (46,95) The values are given for measurements at 296°K. For compounds of the type $A'AU_2O_6$ (A' = Na, K, Rb, Tl, A = Sr, Pb, Ba) the values of μ_{eff} are in the range 1.11 to 1.26 BM. Compounds of the type $M_{0.33}PbU_2O_{5.67}F$ (M = K, Rb, Tl) give μ_{eff} = values from 1.35 to 1.41 BM. Additional values reported are μ_{eff} = 1.32 BM for $NaUO_3F \cdot Pb_2U_2O_7$ and μ_{eff} = 1.21 for $NaUO_3F \cdot 3Pb_2U_2O_7$.

A few results of magnetic susceptibility studies are available for halide compounds of U(V). The value of μ_{eff} for UCl_5 was found to range from 1.05 BM at 77°K to 1.42 BM at 398°K. (94) A value of μ_{eff} of 2.25 BM over the temperature range 200 to 390°K was observed for NH_4UF_6. (69) The magnetic moment of $NaUF_6$ is 2.29 BM in the temperature range 77°K to 453°K. (80).

The magnetic behavior of a series of hexachlorouranates(V) (81) reveals Curie-Weiss dependence from 310°K to temperatures varying

from 140° to 205°K. At the lower temperatures there are marked deviations from Curie-Weiss behavior. The magnetic moments at higher temperatures are 1.62, 1.71, 2.09 and 2.14 BM for the tetramethylammonium, cesium, dimethylammonium and tetraphenylarsonium salts respectively. The authors state that due to the large values of the Weiss constants, -189°, -161°, -388° and -280°, the values of the moments have little significance.

The magnetic moments for UO_2Cl and UO_2Br approach the value of 1.73 BM, the spin-only value for a single electron. (44) The values reported are $\mu_{eff} = 1.86 \pm 0.02$ BM for UO_2Cl and $\mu_{eff} = 1.76 \pm 0.02$ BM for UO_2Br. The suggestion is presented that in these compounds the single electron in a molecular orbital of the UO_2^+ group is under the influence of an important axial field from the uranium-oxygen bond and that this quenches the orbital moment. UO_2F gives a curiously low value of $\mu_{eff} = 1.48$ BM at 296°K. (45)

The sulfide compound, KUS_3, shows Curie-Weiss behavior between 90° and 300°K and $\mu_{eff} = 2.23 \pm 0.02$ BM. (52)

Rudorff and Manzer (94) report that for the addition compound $UCl_5 \cdot SOCl_2$ the values of μ_{eff} range from 1.05 BM at 77°K to 1.29 BM at 293°K. The data appear to favor the 6 d^1 configuration over the 5 f^1 configuration. A value of $\mu_{eff} = 2.13$ BM for $UCl_5 \cdot Ph_3PO$ is considered of little significance due to the large value of the Weiss constant, -270°. (88) The magnetic moment of $UCl_5 \cdot$ TCAC is

1.54 BM at 300°K.(82)

3. Electron Spin Resonance Studies

Only a few studies of electron spin resonance have been reported for U(V) compounds. The ESR spectra of powdered samples of $LiUF_6$, $NaUF_6$ and $CsUF_6$ have been observed at 77°K at 3 cm wavelength. (96) These compounds give a signal in a magnetic field of 9000 gauss. The g values are -0.768, -0.748, and -0.709, respectively. The unsymmetrical signals are expected in powdered samples in which the g tensor is not isotropic. Under the same conditions, complexes, MUF_6 (M = K, Rb, NH_4, Tl, Ag) did not give a signal, except for a weak signal which was considered due to impurity. The absence of an ESR signal for these compounds is thought to be due to large distortions of the octahedra. The results indicate the existance of UF_6^- ions which are axially distorted octahedra. This study was continued (97) to obtain ESR spectra of single crystals of $LiUF_6$, $NaUF_6$ and $CsUF_6$. The paramagnetic resonance absorption of the single crystals was investigated as a function of orientation of the external magnetic field. The authors reported that the UF_6^- ions are axially distorted in these compounds and that in $LiUF_6$ and $CsUF_6$ the deformation axis is the trigonal axis whereas in cubic $NaUF_6$ it is the 111 axis.

The ESR spectra have been obtained for $UCl_5 \cdot TCAC$, $UCl_5 \cdot SOCl_2$, $UCl_5 \cdot PCl_5$, $RbUCl_6$ and $(C_3H_7)_4NUCl_6$. These compounds

gave a very broad signal and the average g values were 1.1 with the sign undetermined. (98) A calculated g value for $UCl_5 \cdot SOCl_2$ is -1.18 and for $[U(OC_2H_5)_5]_2$ the value is -1.16. (5) The agreement between the calculated value and the experimental value for $UCl_5 \cdot SOCl_2$ is quite good.

A determination of the value of g for U(V) ions in a matrix of ThO_2 showed g = 1.25 with the sign undetermined. (99) The value of g is expected to be negative since negative values have been obtained for Pa(IV) and Np(VI) which are isoelectronic with U(V). The value of g for Pa(IV) is -1.14 (100) and the value of g for Np(VI) is -0.61. (101)

ESR spectra have been observed in UF_5 powder, in single crystals of compounds of the type MUF_6 and in single crystals of $NaSbF_6$ doped with U(V). The g values are in the vicinity of -0.7 and some of the signals show splitting. (102)

4. Spectra Studies

a. Vibrational spectra

The infrared spectrum of $NOUF_6$ has a sharp absorption band at 2333 cm^{-1} and a broad intense band split into two absorption maxima at 551 cm^{-1} and 509 cm^{-1}. (75) The maxima at 551 cm^{-1} and 509 cm^{-1} were attributed to the ν_3 vibration of the UF_6^- ion. These absorption maxima are shifted to lower wave numbers by 73 and 114 cm^{-1}, respectively, from the band at 623 cm^{-1} according to the assignment

of Burke, et al. (103) The NO band found at 1876 cm^{-1} in neutral NO is shifted to 2333 cm^{-1} in $NOUF_6$.

In a study of the detailed optical absorption spectrum of $CsUF_6$ Reisfeld and Crosby (104) made the following assignments for the infrared frequencies from vibronic splittings: $A_{1g(\nu_1)}$ = 506 cm^{-1}, $T_{1u(\nu_3)}$ = 503 cm^{-1}, $T_{1u(\nu_4)}$ = 150 cm^{-1}, $T_{2g(\nu_5)}$ = 145 cm^{-1} and $T_{2u(\nu_6)}$ = 100 cm^{-1}.

$N_2H_6(UF_6)_2$ and $N_2H_6UF_7$ show a strong infrared absorption band in the metal-fluorine stretching region at 526 cm^{-1}. (76) This single peak suggests an octahedral structure for UF_6^- and is attributed to the ν_3 frequency of UF_6^-. It is noted that this assignment differs from that of Geichman et al. (75) The difference is considered to be due to differences in cation or in structure. The Raman spectra of $N_2H_6UF_7$, $(NH_3OH)UF_6$ and $CuUF_6$ all show a band at 628 cm^{-1} and it is assigned to the principal symmetric vibration (A_{1g}) of UF_6^-. It should be noted that the assignment of the A_{1g} vibration was to a band at 628 cm^{-1} from Raman spectra but to the 506 cm^{-1} band from vibronic spectral studies.

The infrared spectrum of UO_2Br shows bands at 940, 890 and 850 cm^{-1}. (43) The bands observed for $U(OEt)_5$ are 2990, 2880, 2720, 1455, 1375, 1350, 1130, 1100, 1052, 1025, 908 and 875 cm^{-1}. All the absorption bands except those at 908 and 875 cm^{-1} can be assigned to vibrations arising from the ethoxy radical. (5) These unassigned

bands at 908 and 875 cm^{-1} are in the same region as those observed in UO_2Br at 940, 890 and 850 cm^{-1} and may be U-O vibrations; however, assignments have not been made.

The values obtained for the uranium-chlorine vibrational frequencies for a number of compounds are as follows: $CsUCl_6$, 303 cm^{-1}; $(Me_4N)_3UCl_8$, 310 cm^{-1}; Me_4NUCl_6, 310 cm^{-1}; $(Me_2NH_2)UCl_6$, 308 cm^{-1}; (81) $UCl_5 \cdot Ph_3PO$, 285 cm^{-1}; $UCl_5 \cdot (C_8H_{17})_3PO$, 304 cm^{-1}; (88) $UCl_5 \cdot$ TCAC, 320 cm^{-1}; and Pr_4NUCl_6, 315 cm^{-1}. (98)

The far infrared region has been studied for $CsUF_6$, Et_4NUCl_6 and Et_4NUBr_6. The absorption bands are compared with values deduced for vibronic levels from the observed electronic spectrum. (50) These data and additional data for several of the compounds discussed above are tabulated in the review of uranium(V) chemistry. (18)

The infrared spectra of the addition compounds of the chlorides will be discussed in more detail in connection with the interpretation of the infrared spectra obtained in the present work.

b. Electronic spectra

Analyses of the visible and near infrared spectra and assignments of electronic transitions have been reported for only a few compounds of uranium(V). These reports will be mentioned briefly here and discussed in detail later along with papers presenting calculations for the energy levels for a 5f electron in a cubic ligand field. Reisfeld and Crosby have studied the spectra of

NH_4UF_6, KUF_6, $RbUF_6$ (105) and have done a detailed study of $CsUF_6$. (104) Energy levels have been assigned from the data obtained from the spectra of $UCl_5 \cdot SOCl_2$ and $[U(OC_2H_5)_5]_2$. (5) Ryan has studied the spectra of several UX_6^- salts, X = F, Cl, Br. (50) Electronic and vibronic band assignments have been made for several UCl_6^- salts and for $UCl_5 \cdot TCAC$, $[UCl_5]_2$, and $UCl_5 \cdot SOCl_2$. (98) Energy level assignments have been made for the following ternary oxides of U(V): KUO_3, $RbUO_3$, $KSrU_2O_6F$, $RbSrU_2O_6F$, $KBaU_2O_6F$ and $RbBaU_2O_6F$. (106)

The papers discussed below describe the electronic spectra of some additional U(V) compounds. The spectrum of UO_2^+ has been observed in molten chloride salt solutions over the region 500 to 2000 mμ. The presence of the U(V) species was confirmed by comparison with the spectrum of another $5f^1$ species, NpO_2^{2+}, obtained in $DClO_4$. (107) The spectra show strong resemblance to each other and the peaks in the NpO_2^{2+} spectrum are found at a higher energy than the corresponding peaks of UO_2^+ by an almost constant factor. The UO_2^+ spectrum was also compared with a mull spectrum of $UOCl_3$ obtained at 25°C. The peaks were found to correspond; however, two major peaks at 1070 and 1270 mμ in the spectrum of $UOCl_3$ were absent in the molten salt spectrum. (48) Additional study of the UO_2^+ species in molten salt solution shows that the UO_2^+ spectrum is strongly influenced by solvent and temperature variations, particularly for the shorter wave length regions. (49) The shift of the absorption maxima in

the 625-685 mμ and 800-825 mμ regions toward shorter wave lengths is assumed to be due to an increase in the ligand field strength around the uranium.

The electronic spectrum of UO_2^+ in DMSO (108) over the range 500 to 1600 mμ shows three maxima which correspond to those observed in the molten salt solutions. The main peak is observed at 6620 cm^{-1} with small peaks at 12,940 and 15,080 cm^{-1}. In the molten salt solutions the peaks were found at 6520, 12,500 and 15,080 cm^{-1}. Two weaker peaks observed in the molten salt solutions at 6210 and 6000 cm^{-1} were not observed in the DMSO solution, presumably due to the wide difference in temperature.

A study of a U(V)-U(VI) complex, $U_2O_4^{3+}$ in perchlorate solution reports a band at 7370Å that was observed to disappear as the U(V) disproportionated. (109) This band was not observed in the studies discussed above. It is more than likely that Newton and Baker did not actually have U(V) in solution.

The series of complexes having $MF:UF_5$ ratios (M = NH_4, Li, Na, K, Rb, Cs) of 1:1, 2:1 (except Li and Na) and 3:1 (except Li) all show intense absorption lines in the 1.3μ (7,700 cm^{-1}) to 1.5μ (6,640 cm^{-1}) region. (72,73) It was found that KUF_6, NH_4UF_6 and $RbUF_6$ give a single sharp band at 1.42μ (7.042 cm^{-1}). X-ray evidence has shown that these three compounds are isostructural and of very nearly the same size. The band is split

into three components for $LiUF_6$, $NaUF_6$ and $CsUF_6$. The X-ray powder diffraction patterns reflect the differences from the three compounds.

The report of electronic spectral properties of $HUF_6 \cdot 2.5H_2O$ describes a prominent absorption at 1.36μ (7,353 cm^{-1}) whereas that of $HUF_6 \cdot 1.25H_2O$ has the main peak in this region shifted 25Å (14 cm^{-1}) toward longer wave lengths. The comparison of the spectra of these compounds with those of the anhydrous salts $LiUF_6$, $NaUF_6$ and $CsUF_6$ shows that nearly identical spectra are obtained. The similar spectrum obtained for the U(V) species in aqueous HF is indication of the existence of the UF_6^- species in the aqueous solution. (70) The existence of the UF_6^- species is supported by the work showing the existence of pentavalent niobium in fluoride solutions as NbF_6^-. (110, 111)

The solution spectra have been reported for the following compounds: $UCl_5 \cdot SOCl_2$, Me_4NUCl_6, $(Me_4N)_3UCl_8$, $UCl_5 \cdot Ph_3PO$, $UCl_5 \cdot (C_8H_{17})_3PO$ and $CsUCl_6$. (81,88)

C. Research Goals

The goal of the present research program has been to prepare, characterize and carry out spectral studies of new coordination compounds of uranium(V). As has been noted only a few examples of halide addition compounds have been prepared and only F^-, Cl^- and O^{2-} and oxygen and nitrogen donor ligands have

complexed to uranium(V) heretofore.

It has been found in this study that the reaction

$$UCl_5 \cdot TCAC + xL \rightarrow UCl_5 \cdot xL + TCAC \qquad (26)$$

can be carried out in benzene solution with a variety of ligands to produce compounds, $UCl_5 \cdot xL$. Compounds of this type which have been prepared are $UCl_5 \cdot Ph_3P$, $UCl_5 \cdot$ diphos, $UCl_5 \cdot 2C_9H_7NO$ and $UCl_5 \cdot 4C_9H_7NO$.

A different type of reaction occurs when the ligand tropolone reacts with a solution of $UCl_5 \cdot TCAC$. Tropolone, $C_7H_5O_2H$, is a potential bidentate ligand which may lose a proton and coordinate as a monoanion. In the present case TCAC and one chlorine are replaced and the resulting compound is $UCl_4T \cdot 4HT$.

Reactions of other ligands with $UCl_5 \cdot TCAC$ have produced the first ionic compounds. The ionic compounds which have been prepared are $[UCl_4dipy]Cl$, $[U_2Cl_9(Ph_3As)]Cl$ and $[U_2Cl_9(Ph_3Bi)]Cl$.

In addition to the compounds listed above other unstable and impure compounds were isolated containing ethylene<u>bis</u>diphenylarsine, triphenylstibine, diphenylsulfoxide, o-phenanthroline, ethyl diphenylphosphinite and diethylphenylphosphonite.

The new compounds have been characterized by elemental analyses, conductance measurements and magnetic susceptibility measurements whenever a sufficient quantity of the compound was obtained to allow this latter measurement to be made by the Gouy method.

The compounds are all extremely sensitive to moisture and oxygen and preparations of the compounds and subsequent studies were carried out under an argon atmosphere and in anhydrous, oxygen-free solvents. The compounds containing nitrogen donor ligands are especially unstable toward oxygen and moisture and are decomposed within seconds on contact with air. The compounds containing phosphorous and arsenic donor ligands are somewhat more stable but decompose within minutes on contact with oxygen or moisture. The tropolone complex, $UCl_4T \cdot 4HT$ is surprisingly stable and it requires several days for it to decompose in dry air. However, the compound is immediately decomposed by water and organic solvents. Curiously, it does not give a stable solution in anhydrous nitromethane as has been noted for some of the other compounds. It may be that the solid is stabilized by the presence of the excess tropolone, but that when dissolution occurs this stabilizing factor is removed.

The electron spin resonance spectrum has been obtained for each of the compounds except $[U_2Cl_9(Ph_3As)]Cl$, for which a powdered sample of the compound did not produce a signal. The different type spectra obtained for the various compounds will be correlated with the suggested structure of the compounds.

As has been noted, the visible and near infrared spectra have been analyzed for only a few uranium(V) compounds. A primary interest in the preparation of new coordination compounds of uranium(V)

has been to obtain visible and near infrared spectra of these compounds and to study the effect of different ligands and structure on the spectra. The visible and near infrared spectra have been obtained for all compounds in Nujol mulls at 77°K over the region 4,000 to 25,000 cm^{-1}. Solution spectra have been obtained for the compounds which are sufficiently soluble and which form stable solutions. The spectra are interpreted for the various compounds with different ligand fields and different symmetries.

The infrared spectra have been obtained for all compounds in Nujol mulls from 4000 to 300 cm^{-1} and for some of the compounds from 4000 to 200 cm^{-1}. The presence of the ligand in the compound is confirmed and some information on the nature of bonding is obtained from the spectra. Tentative assignments of U-P and U-N bands have been made and more firm assignments have been made for the U-Cl and U-O bands.

The new compounds prepared here include the first uranium(V) compounds containing U-P, U-As and U-Bi bonds and the first well characterized compound containing a U-N bond. Furthermore, some new types of compounds are represented by those compounds in which a ligand molecule has replaced a chlorine atom from the UCl_5 unit.

CHAPTER II

EXPERIMENTAL PROCEDURES

A. Materials, Apparatus and Methods of Analysis

The compounds of uranium(V) which have been prepared are quickly decomposed by oxygen and moisture except for $UCl_4T \cdot 4HT$ which is stable in dry air for a few days. The preparation and studies of the compounds were done in a glove bag filled with argon or in closed glass vessels filled with argon. The preparation and studies of $UCl_5 \cdot Ph_3P$ and $[UCl_4dipy]Cl$ were carried out in a steel dry box under an atmosphere of dry, oxygen-free nitrogen.

All solid chemicals used were vacuum dried before use. The solvents used were dried, distilled under nitrogen or dried, distilled and the dissolved oxygen removed by bubbling argon through the solvent for several minutes.

The analyses for uranium were done by reduction of the uranium(V) to uranium(IV) using a Jones Reductor followed by titration to uranium(VI) with standard potassium dichromate solution.

The chloride analyses were done by Volhard titration, by gravimetric determination as silver chloride or were done by a commercial laboratory. The method of analysis chosen was determined by the nature of the compound. Analyses for carbon, hydrogen and nitrogen were done by Mr. Ralph Seab, a staff member of the LSU Chemistry Department. Analyses of P and As were obtained from a commercial laboratory.

B. Preparation and Characterization of Compounds

1. UCl_5·TCAC [Pentachloro(trichloroacrylylchloride)uranium(V)]

The procedure for preparation of UCl_5·TCAC is a modification of the procedure used by Ortego.(82) Technical grade hexachloropropene obtained from Columbia Organics was distilled and the fraction distilling between 208-210°C was collected for use. The U_3O_8 to be used in the reaction was ignited to red heat just before use. The 17 grams of U_3O_8 was added to 160 ml of hexachloropropene and the mixture heated with stirring. The temperature was slowly increased to 95°C and kept between 95-100°C. In some preparations the reaction occurred at this temperature after about 1 hour. In other preparations the temperature was maintained between 95-100°C for two hours and no reaction occurred. When the temperature was then increased to about 105°C, the reaction occurred and continued for about 30 minutes. The reaction is slightly exothermic but heat is necessary to maintain the temperature needed for the reaction. The reaction is characterized by the evolution of gases (most likely Cl_2 and ClO_2) and the appearance of a deep red color which is characteristic of UCl_5·TCAC in solution. After the reaction subsides the red solution is transferred to a dry, argon-filled flask and argon is bubbled through the solution. Almost immediately red-orange crystals begin to form. Argon gas is bubbled through the solution for several minutes and it is then left standing in an ice bath for about two hours. The red-orange crystals are filtered under argon and washed with anhydrous CCl_4. After drying under vacuum, the compound is stored in a glass container under argon.

The compound may be kept for several months in this way. The compound has a sharp characteristic odor, and decomposes in seconds on contact with air producing a dark green substance.

As is indicated in the foregoing procedure the course of the reaction is variable. It is a slow reaction but the course of the reaction must be constantly observed because some heat is liberated and periodically this may result in a sharp increase in temperature above 110°C. When the temperature is allowed to go above 110°C a mixture of products is usually obtained. The commercial source of the hexachloroprene also seems to be an important factor and the best results were obtained using hexachloropropene obtained from Columbia Organics.

2. Preparation of Nitrogen Donor Complexes

[UCl_4dipy]Cl Tetrachloro-2,2′-dipyridyluranium(V)chloride

A benzene solution of UCl_5·TCAC was prepared by dissolving 2.3 millimoles in about 50 ml of benzene. The solution has the characteristic deep red color of UCl_5·TCAC. A dark green residue always remains when this solution is prepared. This impurity is thought to be UCl_4 which unavoidably is formed during the preparation of the UCl_5·TCAC. The procedure for the preparation of UCl_5·TCAC involves stopping a reaction, which would ultimately yield UCl_4, at an intermediate stage. The residue is removed from the solution by filtration. A solution of 8.3 millimoles of 2,2′-dipyridyl was dissolved in about 20 ml. of benzene. About half of this solution was added to the solution of UCl_5·TCAC and an immediate reaction occurred producing a precipitate. The red color in the solution

persisted and so additional 2,2′-dipyridyl was added. The precipitate on the walls of the flask appeared yellow but the bulk of the precipitate in solution appeared to have a red tint. After stirring for several minutes the supernatant benzene was decanted off and fresh benzene was added. The precipitate was stirred for several minutes and as the particle size became smaller the red color disappeared. The precipitate was filtered and washed with several small portions of C_6H_6 and then dried overnight under vacuum. This compound is extremely unstable to air and moisture. Several attempts were made to prepare the compound but after obtaining the product it was lost during filtration or drying. The successful preparation was achieved by doing all of the work in a steel dry box. The yellow compound is stable under dry nitrogen or argon.

The melting point was obtained in a sealed tube. At 205°C the compound turned brown and at 215°C white crystals appeared on the surface of the dark solid. At 270°C the dark solid melted. The differential thermal analysis curve showed small endothermic peaks at 228°C and 289°C. The peak at 228°C probably corresponds to the loss of the white crystalline material which was observed on taking the melting point. It is assumed this white crystalline material is the 2,2′-dipyridyl separating from the compound.

The equivalent conductance of a 1.4×10^{-4} M solution of this compound in nitromethane was 112. For a 1.196×10^{-3} M solution of $(C_2H_5)_4NI$ in nitromethane the equivalent conductance is reported as 104.(112) The value obtained for the equivalent conductance indicated that the complex with 2,2′-dipyridyl is a 1:1 ionic

compound. It is assumed that the dipyridyl has replaced one chlorine in the UCl_5 group and that this chlorine is ionic. The six-coordinate compound would therefore be expected to have the formula $[UCl_4dipy]Cl$.

Analysis. Observed: U 40.13, Cl 26.93, C 22.42, H 1.98, N 4.98

Calculated for $UCl_5 \cdot C_{10}H_8N_2$: U 41.65, Cl 31.02, C 21.02, H 1.41, N 4.82

$UCl_5 + C_{12}H_8N_2$ (Formula for compound not established).

Two attempts were made to prepare a complex by the reaction of o-phenanthroline with $UCl_5 \cdot TCAC$. In both cases the immediate reaction product was a yellow-tan precipitate. In both cases the product decomposed before it could be filtered. No further work was done with this ligand as another member of the research group was attempting to prepare a compound with o-phenanthroline.

3. Preparation of Phosphorus Donor Complexes

$UCl_5 \cdot Ph_3P$ [Pentachloro(triphenylphosphine)uranium(V)]

A solution of 4.58 millimoles of Ph_3P in 25 ml. of C_6H_6 was added to a solution containing ~ 2.4 millimoles of $UCl_5 \cdot TCAC$. An immediate reaction was indicated by the loss of the red color of the $UCl_5 \cdot TCAC$ solution and the formation of a fluffy, light green precipitate. The solution was stirred for about 10 minutes, the precipitate washed by decantation with benzene and then filtered and washed with several small portions of benzene. The precipitate was dried under vacuum and stored under dry nitrogen in the dry box. The compound is a medium green color. An attempt to determine the

melting point showed that the compound begins to darken about 140°C, looks wet at 190°C and becomes very dark at 242°C, but does not melt up to 300°C. Conductance measurements made in nitromethane show that this compound is not ionic. The compound is found to be insoluble in non-polar solvents and decomposed by many solvents. It is very slightly soluble in nitromethane.

Analysis observed: U 36.22, Cl 24.07, C 31.90, H 3.03, P 3.95.

Calculated for $UCl_5 \cdot Ph_3P$: U 35.13, Cl 26.16, C 31.91, H 2.23, p 4.57

$UCl_5 \cdot (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ [Pentachloro{ethylenebis(diphenyphosphine)}-uranium(V)]

A benzene solution of UCl_5·TCAC was prepared which contained approximately 2 millimoles in 35 ml. of benzene. A benzene solution of the diphos ligand was prepared by dissolving 3.09 millimoles of it in about 25 ml. of benzene. Immediately upon the addition of the diphos solution to the UCl_5·TCAC solution a green precipitate began to form and by the time all the diphos solution had been added, the red solution color had completely disappeared. The solution was stirred for about 15 minutes and then filtered under vacuum. The precipitate was washed with several small portions of benzene and then dried overnight under vacuum. The dry compound which has a very pale green color was stored under argon.

The compound is insoluble in non-polar solvents and is decomposed by a number of solvents. It is slightly soluble in anhydrous nitromethane. The compound darkens when heated to 200°C

but does not melt up to 300°C. Differential thermal analysis showed no endothermic or exothermic peaks up to 500°C. Conductance measurements in nitromethane show that the compound is not an ionic species.

Analysis observed: U 28.68, Cl 20.43, C 38.18, H 3.30, P 6.77

Calculated for $UCl_5 \cdot (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$: U 29.25, Cl 21.79, C 38.37, H 2.97, P 7.61

UCl_5+$C_6H_5P(OC_2H_5)_2$ (Formula for compound not established.)

A solution of approximately 1.2 millimoles of UCl_5·TCAC in 50 ml. of benzene was prepared. About 2 ml. (10 millimoles) of diethylphenylphosphonite was mixed with 20 ml. of benzene and this solution was then added to the solution of UCl_5·TCAC. An immediate reaction occurred as evidenced by the loss of the red color due to UCl_5·TCAC and the appearance of a light green color in the solution. After a few minutes a dark green oil had separated from the solution. The mixture was stirred overnight; however, no change in the green oil was observed. The benzene was removed by vacuum evaporation but the green oil remained and no solid product was obtained. The green color, which has also been observed for the other phosphorous donor compounds, indicates that a complex has been formed by this reaction, but it could not be isolated as a solid and purified.

UCl_5+$(C_6H_5)_2POC_2H_5$ (Formula for compound not established).

A solution containing approximately 1.5 millimoles of UCl_5·TCAC was prepared. About 1 ml. (approximately 5 millimoles) of ethyldiphenylphosphinite was added directly to the solution of

UCl_5·TCAC. This was a slight excess over the amount necessary to cause the loss of red color from UCl_5·TCAC in the solution. As the $(C_6H_5)_2POC_2H_5$ was added the solution immediately turned a light green and in a few minutes a darker green oil separated from the solution. The mixture was stirred for several days but no solid product was obtained. The green color indicates that a complex with uranium has been formed.

4. Preparation of Arsenic Donor Complexes

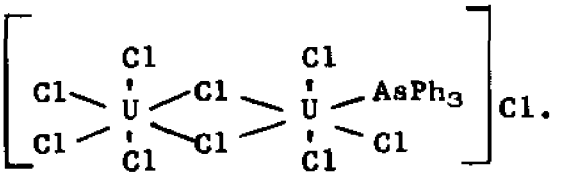
$[U_2Cl_8(Ph_3As)Cl]$ Tetrachlorouranium(V)-μ-dichloro-trichloro-(triphenylarsine)uranium(V) chloride

Two preparations of this compound were made using benzene as the solvent. Because of poor yields a third preparation was made using toluene as the solvent. A toluene solution of UCl_5·TCAC was prepared by dissolving ~1.5 millimoles in 40 ml. of toluene. The deep red color which is so characteristic of UCl_5·TCAC solutions is the same as noted for benzene solutions. The solution of Ph_3As was prepared by dissolving 4.38 m mole of the compound in 25 ml. of toluene. Upon mixing the solutions, there was an immediate reaction which produced a light green precipitate. The reaction mixture was stirred overnight, filtered and washed with benzene. When dry the pale green compound was stored under argon. The product obtained appears to be the same and gives the same analysis whether the reaction mixture is filtered after about 3 hours or after 20 hours.

On heating, the pale green color of this compound changed to light brown at about 130°C. It appeared that some portion of the

compound had been volatilized at this temperature. The color became dark brown at 190°C and this dark residue did not melt up to 300°C.

The equivalent conductance of a 7.05×10^{-5} M solution of this compound was 86.3 mhos. The equivalent conducatnce of a 1.196×10^{-3} M solution of $(C_2H_5)_4I$ in nitromethane is 104.(112) The equivalent conductance value is considered evidence that $[U_2Cl_8Ph_3As]Cl$ exists as a 1 to 1 electrolyte. The very large size of the cation in this compound would probably cause the equivalent conductance to be somewhat lower than is observed for $(C_2H_5)_4NI$. The structural formula suggested for this compound is



The analysis for chlorine in this compound was low. This analysis was obtained from a commercial laboratory and apparently their method of analysis was not suitable to this type of compound. Low chlorine analyses have been obtained by the Gailbraith Laboratories for other compounds in this work and by other workers in this laboratory for chlorine in similar types of coordination compounds.

Analysis. Observed: U 42.41, Cl 23.74, C 20.60, H 2.07, As 7.97

Calculated for $[U_2Cl_8(Ph_3As)]Cl$: U 41.88, Cl 31.18, C 19.02, H 1.33, As 6.59

$UCl_5 \cdot TCAC + (C_6H_5)_2As(CH_2)_2As(C_6H_5)_2$ (Exact formula of compound not established)

The reaction of a benzene solution containing ~ 0.40 millimole of $UCl_5 \cdot TCAC$ in 30 ml. of benzene with 0.35 millimole of

ethylenebis(diphenylarsine) immediately produced a light green precipitate. The reaction mixture was stirred for an hour, filtered, washed with benzene and dried under vacuum. The pale green compound was stored under argon.

Analysis of the compound showed that it contained 19.95% C and 2.28% H. The calculated percentage of carbon for the formula $(UCl_5)_2L$ is 23.64. The observed percentage of carbon is too low for any formula which can be considered a reasonable possibility. Because of the indication of incomplete reaction no further attempts were made to prepare the compound. The electronic spectrum indicated that the product was some sort of a uranium(V) species.

5. Preparation of an Antimony Donor Complex

$UCl_5 \cdot TCAC + Ph_3Sb$ (Exact formula of compound not established)

A solution containing 3.5 millimoles of Ph_3Sb in 50 ml. of benzene was added to a solution containing 1 millimole of $UCl_5 \cdot TCAC$ in 40 ml. of benzene. An immediate reaction occurred and produced a finely divided, pale green precipitate. The product was filtered, washed with benzene, dried under vacuum and stored under argon. The yield of this compound was very low. Analysis showed the compound contained only 6.91% carbon and 1.66% hydrogen. The amount of carbon present was too low to represent the percentage of carbon in any reasonable compound which could be formulated. The compound was slightly soluble in nitromethane. Because of the low yield of product and indication of incomplete reaction no further attempts were made to prepare this compound. However, the electronic spectrum and the ESR spectrum indicated the product

obtained did contain a uranium(V) compound. It is thought that the impurity present in this compound is $(UCl_5)_2$. This high molecular weight impurity could account for the very low carbon analysis.

6. Preparation of a Bismuth Donor Complex

$[U_2Cl_8(Ph_3Bi)Cl]$ Tetrachlorouranium(V)-μ-dichloro-trichloro-(triphenylbismuthine)uranium(V) chloride

A solution containing ~1.5 millimoles of UCl_5·TCAC in 25 ml. of benzene was prepared. A suspension of 3.11 millimoles of triphenylbismuthine in 50 ml. of benzene was added to the UCl_5·TCAC solution. The solution was stirred as the triphenylbismuthine was added and the formation of a light green precipitate occurred immediately on the addition of the triphenylbismuthine. The mixture was stirred about 30 minutes and then the supernatant benzene was decanted and fresh benzene added and the mixture stirred several minutes. The product was filtered and washed with several small portions of benzene. The pale green compound was vacuum dried and stored under argon.

An attempt to determine the melting point resulted in decomposition of the compound. The compound turned dark brown at 190°C and this dark residue did not melt up to 300°C.

The equivalent conductance of a 4.41×10^{-5} M solution of this compound in nitromethane is 136. This is somewhat higher than the value reported for a 1.196×10^{-3} M solution of $(C_2H_5)_4NI$ solution in nitromethane.(112) The value for the equivalent conductance of the triphenylbismuth complex may be higher because the

solution is more dilute. The compound is assumed to be a 1 to 1 electrolyte and analogous to $[U_2Cl_9Ph_3As]Cl$.

The chlorine analysis obtained for this compound is low and it was obtained from the same laboratory as the chlorine analysis for the triphenylarsine complex discussed above. The problem may be due to difficulty in completely decomposing the complex without causing loss of the chlorine. The commercial laboratory reported that it could not do a bismuth analysis.

Analysis. Observed: C 15.19, H 1.41, Cl 17.34

Calculated for $[U_2Cl_9Ph_3Bi]Cl$: C 16.99, H 1.92, Cl 27.87.

7. Preparation of an Oxygen Donor Complex

$UCl_4T \cdot 4HT$ [Tetrachloro(troplono)tetratropoloneuranium(V)]

A solution of 10.9 millimoles of tropolone in 25 ml. of benzene was added to a solution containing ~ 2.5 millimoles of $UCl_5 \cdot TCAC$. An immediate reaction occurred producing a finely divided, black precipitate. The mixture was stirred overnight, the supernatant benzene decanted and fresh benzene added. After this mixture had been stirred about 30 minutes the compound was filtered, washed with several small portions of benzene and vacuum dried. The compound was stored under argon. This compound is the only complex prepared which is stable in air for more than a few minutes. This compound can be exposed to air for several days before any change in color occurs in contrast to the other compounds which change color in seconds or minutes. The black $UCl_4T \cdot 4HT$ changes to a rather bright orange after being exposed to dry air for about 3 weeks.

This compound is quickly decomposed by most solvents. It appears to be slightly soluble in nitromethane but decomposes within a few minutes in this solvent.

Conductance measurements of a nitromethane solution indicate that this compound is not ionic.

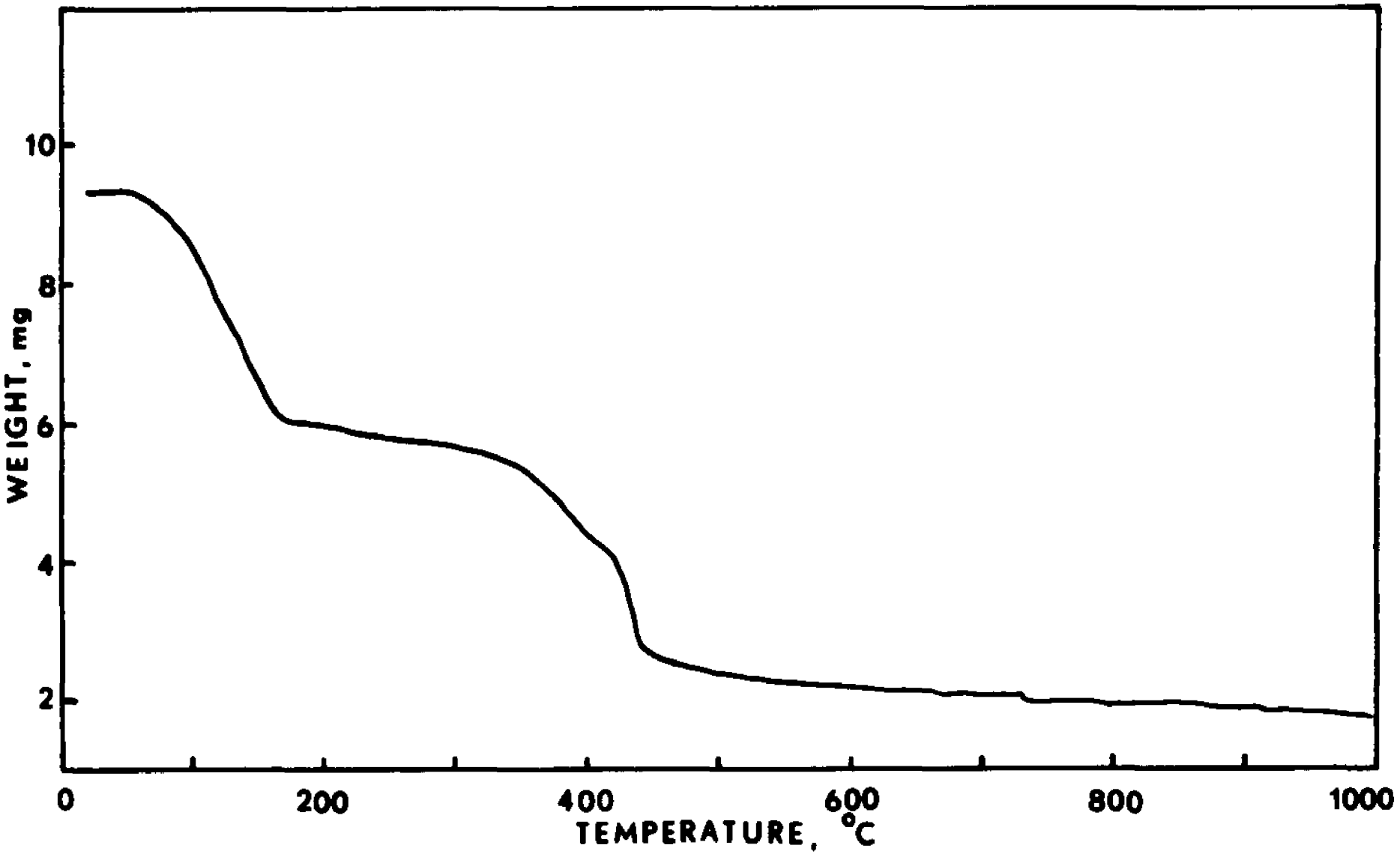
The differential thermal analysis curve of this compound showed a sharp endothermic peak at about 207°C. The melting point obtained in a sealed tube was 125°C.

A thermogravimetric analysis of this compound gave some interesting results. The thermogravimetric analysis curve is shown in Figure 1. The effluent from the furnace of the TGA instrument was passed through a weakly basic solution in an effort to determine whether the tropolone or chloride ions would be lost first by the compound during the heating process. The weight loss which had occurred at 180°C corresponds to 35.9% of the initial weight. The weight of 3HT would represent 37.5% of the total weight. The solution through which the effluent was passed was tested for the presence of chloride ion by acidifying the solution and adding a solution of silver nitrate. The solution obtained gave no evidence for the chloride ion until the temperature reached 180°C. Each portion tested after this temperature gave the test for the chloride ion. The weight loss which occurred between 180°C and 450°C is 35.3% of the total weight and appears to represent the loss of HT,T^- and $3Cl^-$. The weight of HT,T^- and $3Cl^-$ would be 35.5% of the total weight. The weight loss between 450°C and 550° represents approximately the loss of 1 Cl^-. The exit tube

FIGURE I

Thermogravimetric Analysis Plot

for $UCl_4T \cdot 4HT$


WEIGHT, mg
10
8
6
4
2
0
200
400
600
800
1000
TEMPERATURE, °C

from the furnace was found to have some white crystals on the top surface at the conclusion of the analysis. These had the characteristic odor of tropolone and melted at 51°C. The recorded melting point of tropolone is 49-50°C. The lower surface of the exit tube showed the presence of some dark material and it appears that some uranium was lost during the heating at higher temperature. The results of this study indicate that the compound first loses 3HT, then 1 HT and T^- along with $3Cl^-$ and finally 1 Cl^-.

Analysis. Observed: U 24.22, Cl 13.84, C 43.80, H 3.54.

Calculated for $UCl_4T \cdot 4HT$: U 24.06, Cl 14.33, C 42.45, H 2.95

UCl_5+Ph_2SO (Exact formula of compound not established)

A solution containing approximately 1.5 millimoles of $UCl_5 \cdot TCAC$ in 50 ml. of benzene was prepared. A solution containing 7.1 millimoles of Ph_2SO in 50 ml. of benzene was added to the red solution of $UCl_5 \cdot TCAC$. The solution immediately turned a pale yellow. Closer examination revealed that a reddish-brown oil was present in the solution. After the mixture had been stirred overnight the oil was found to have solidified on the walls of the flask. The benzene was poured off and the solid scraped from the walls of the flask. The brown solid was dried by vacuum evaporation. The product was a light yellow-brown when dry. Analysis of the compound showed it contained 40.14% C and 3.04% H. It was not possible to arrive at

any reasonable formula to fit this analysis. No further work was done with this ligand.

8. Preparation of Nitrogen-Oxygen Donor Complexes

$UCl_5 \cdot 2C_9H_7NO$ Pentachlorobis(8-hydroxyquinoline)uranium(V)

Approximately 1.7 millimoles of UCl_5·TCAC was dissolved in 60 ml. of benzene and approximately 3 millimoles of 8-hydroxyquinoline added to the solution. An immediate reaction occurred and produced a dark brown, finely divided precipitate. The reaction mixture was stirred overnight and then the precipitate was filtered, washed with CCl_4 and dried under vacuum.

This dark brown compound is extremely sensitive to moisture and oxygen. Because this compound was quickly decomposed by solvents it was not possible to prepare a solution of this complex.

When heated under vacuum a light colored solid sublimed at about 120°C leaving a residue which is slightly lighter in color than the original compound. When an attempt was made to determine the melting point the compound appeared to decompose at about 200°C and the dark residue did not melt up to 300°C.

Analysis. Observed: C 30.67, H 2.61, Cl 22.94

Calculated for $UCl_5 \cdot 2C_9H_7NO$: C 30.68, H 1.86, Cl 25.15

$UCl_5 \cdot 4C_9H_7NO$ Pentachlorotetrakis(8-hydroxyquinoline)uranium(V)

A solution containing approximately 2 millimoles of UCl_5·TCAC in 40 ml. of benzene was prepared. A benzene solution of 8.1 millimoles of 8-hydroxyquinoline was added to the solution of

UCl_5·TCAC. An immediate reaction produced a finely divided, brown precipitate. The mixture was stirred overnight in an attempt to increase the particle size of the precipitate prior to filtration. The brown precipitate was filtered, washed with benzene and dried under vacuum. When dry this compound had a tan color compared to the dark brown of $UCl_5 \cdot 2C_9H_7NO$.

When heated in order to determine the melting point, this compound turned a dark reddish-brown at 230°C. This dark substance did not melt up to 300°C.

A measurement of the conductivity of a nitromethane solution of this compound indicated that it is not an ionic species.

This compound is extremely unstable to moisture and oxygen. It is decomposed very quickly by most solvents. A nitromethane solution proved to be stable for a short time.

Analysis. Observed: U 24.99, Cl 17.15, C 42.80, H 2.88, N 5.69

Calculated for $UCl_5 \cdot 4C_9H_7NO$: U 23.89, Cl 17.79, C 43.39, H 2.83, N 5.66

C. Equivalent Conductances

The equivalent conductance of solutions of uranium compounds were calculated from the measured resistances of 10^{-3} to 10^{-5} M solutions. Resistance measurements were made by use of an Industrial Instruments model RC 16 conductivity bridge operating at 60 c.p.s. A cell constant for the conductivity cell was determined by using a standard potassium chloride solution.

D. Magnetic Susceptibility Measurements

Magnetic susceptibility measurements of compounds were determined by the Guoy method on an Ainsworth type BCT balance with an Alpha Scientific Lab., Inc. model Al 7500 electromagnet. Measurements were made at room temperature. Hydrated ferrous ammonium sulfate and mercury tetrathiocyanatocobaltate(II) were used for calibration of the sample tube. All values were corrected for diamagnetism of the ligands and metal ion.

E. Electron Spin Resonance Spectra

The electron spin resonance spectra of the compounds were recorded on a model Jes-3BX, X band spectrometer made by Japan Electron Optics Laboratory Co., Ltd. The spectra were obtained at room temperature. The compound was placed in the sample tube in an argon atmosphere and the sample tube sealed as protection from oxygen and moisture.

F. Vibrational Spectra

Infrared spectra were recorded in the 600-4000 cm^{-1} region on a Beckman IR-7 or Beckman IR-10 spectrophotometer. For the far infrared region (200-600 cm^{-1}) a Beckman IR-10 or Beckman IR-7 fitted with CsI optics was used. Nujol mulls pressed between NaCl plates were used in the sodium chloride region and Nujol mulls between CsI plates were used in the far infrared region. The mulls were placed between the plates in the glove bag and then the edges of the plates were covered with Scotch tape to try to protect the mull from

air and moisture. The mull was kept under argon until it was placed in the instrument.

G. Electronic Spectra

The visible and near-infrared spectra were recorded over the region 4000 to 25,000 cm^{-1} on a Cary 14R spectrophotometer. The spectra were obtained using Nujol mulls on filter paper at 77°K for all compounds. The filter paper with the mull was mounted on a brass plate in an argon atmosphere and then quickly immersed in an optical dewar containing liquid nitrogen. Room temperature spectra of some of the compounds were obtained using Nujol mulls smeared on filter paper. A sample of Nujol on filter paper was used as a reference in obtaining the spectra of mulls as described above. Solution spectra for some compounds was obtained using 1, 5 or 10 cm matched quartz cells.

H. Mass Spectra

The mass spectra of $UCl_5 \cdot Ph_3P$, $U_2Cl_9(Ph_3As)$ Cl, $UCl_4T \cdot 4HT$ and $UCl_5 \cdot 4C_9H_7NO$ were obtained by Mrs. Cheryl White, a staff member of the LSU Chemistry Department. The instrument used is a Varian M-66 manufactured by Varian Associates.

CHAPTER III

RESULTS AND DISCUSSION

A. Magnetic Susceptibility Data

In the Guoy method for the determination of magnetic moment a cylindrical powdered sample of cross section A is suspended from a balance between the poles of a magnet. The lower end of the tube is in a strong field, H, while the upper end is in a negligible field, Ho. The force acting on the sample is given by the following equation:

$$F = \tfrac{1}{2}A(H^2-H_o^2)(K-K')+S \qquad (26)$$

K is the magnetic susceptibility of the sample per unit volume, K′ is the magnetic susceptibility of the atmosphere per unit volume and S is the force due to the sample tube. The force is measured by first counterpoising the sample without the magnetic field and then adding weights to restore the balance after the magnetic field has been applied. For a sample of uniform cross-section, $\tfrac{1}{2}A(H^2-H_o^2)$ will be a constant. The gram susceptibility is related to the volume susceptibility by a constant, the density. Equation 26 can thus be expressed

$$X_g = \frac{B \times F'}{W} \qquad (27)$$

In this equation B is the tube calibration constant, $F' = F-S$, X_g is the gram susceptibility and W is sample weight in grams. The

calibration constant B is determined by using a substance of known magnetic susceptibility. The molar susceptibility, X_m, is obtained by multiplying the gram susceptibility by the molecular weight of the sample.

The molar susceptibility for a compound will include contributions from paramagnetic and diamagnetic susceptibilities. The measured molar susceptibility for a metal ion complex may be represented in the following way

$$X_m = X_m' + X_m(\text{ligands}) + X_m(\text{ions}) \tag{28}$$

X_m' is the paramagnetic susceptibility of the metal ion, X_m (ligands) and X_m (ions) are the diamagnetic susceptibility of the ligands and ions present in the compound. X_m' is calculated by

$$X_m' = X_m - X_m(\text{ligands}) - X_m(\text{ions}) \tag{29}$$

The correction is positive since the values for diamagnetic susceptibility are negative. The magnetic moment in Bohr magnetons is then calculated by the following equation:

$$\mu_{eff} = 2.84(X_m'T)^{\frac{1}{2}} \tag{30}$$

T is the absolute temperature at which the magnetic susceptibility is determined.

Magnetic susceptibility measurements have been made for $UCl_5 \cdot$diphos, $UCl_5 \cdot 2C_9H_7NO$, $UCl_5 \cdot 4C_9H_7NO$, $UCl_4T \cdot 4HT$, $[U_2Cl_9(Ph_3As)]Cl$ and $[UCl_4dipy]Cl$. The calculated magnetic moments of these compounds are given in Table I. The values obtained for the magnetic moments

TABLE I

MAGNETIC MOMENTS FOR URANIUM(V) COMPOUNDS

Compound	T(^{o}K)	μ_{eff}(BM)
$UCl_5 \cdot diphos$	298.5	2.76
$UCl_5 \cdot 2C_9H_7NO$	297	1.95
$UCl_5 \cdot 4C_9H_7NO$	303	2.84
$UCl_4T \cdot 4HT$	301	1.94
$[U_2Cl_9(Ph_3As)]Cl$	299	3.40 or 1.70 per U^{5+}
$[UCl_4dipy]Cl$	298	2.78

of the different compounds show considerable variation. The values may be compared with a value of μ_{eff} of 2.25 BM for NH_4UF_6,(69) 1.86 BM for UO_2Cl(44) and 1.54 BM for $UCl_5 \cdot TCAC$.(82) A review of the literature survey section of magnetic moment data reveals that values reported for different types of uranium(V) compounds have covered a range of value from 2.25 to 1.06 BM.

The calculated value of μ_{eff} for $[U_2Cl_8Ph_3As]Cl$ is 3.40 BM. This gives a value of μ_{eff} = 1.70 BM per U^{5+}. This result supports the suggested dimeric structure for this compound.

B. Electron Spin Resonance Spectra

Electron spin resonance, sometimes termed electron paramagnetic resonance, is the branch of absorption spectroscopy in which radiation of microwave frequency is absorbed by molecules which have electrons with unpaired spins. For an electron with spin $s = \frac{1}{2}$, the spin angular momentum quantum number can have values $m_s = \pm \frac{1}{2}$. In the absence of a magnetic field these spin energy states are degenerate, however, when a magnetic field is applied the degeneracy is removed. The state with the spin magnetic moment aligned with the field is the low energy state and corresponds to the quantum number $m_s = -\frac{1}{2}$. The state with the spin magnetic moment opposed to the applied field is the high energy state and corresponds to the quantum number $m_s = +\frac{1}{2}$.

The application of an oscillating field perpendicular to the applied magnetic field induces a transition provided the applied frequency satisfies the resonance condition. The energy of the

transition is $E = h\nu$ as in other forms of absorption spectroscopy. For electron spin resonance the resonance condition is

$$h\nu = g\beta H \tag{31}$$

In equation 31 h is Planck's constant, ν is the frequency of radiation, β is the Bohr magneton, H is the field strength and g is the spectroscopic splitting factor.

The lower energy state, N_1, has a greater population than the higher energy state, N_2, and in general the distribution is given by the Maxwell-Boltzman expression

$$\frac{N_2}{N_1} = \exp(-\frac{h\nu}{kt}) \tag{32}$$

where h and ν are as defined above and k is the Boltzman constant and T the absolute temperature. At room temperature and with an energy separation corresponding to a wavelength of 8.6 mm the ratio is 0.995.(113)

In order for absorption of radiation to continue, there must be a means by which electrons from the higher energy state lose energy and drop back to the lower energy state. A mechanism is needed in which there is a transfer of energy by interaction with some system other than the incident radiation and such a mechanism is termed a relaxation process.

For a field strength of 10,000 gauss the resonance frequency of a free electron is 28,026 Mc/sec. This frequency has a wavelength of approximately 1 cm. An X band spectrometer operates at about 3 cm

wavelength with ν = 9,500 Mc/sec. For this frequency the field required for resonance for a free electron is about 3,400 gauss.(114) An ESR spectrum could be obtained by varying the frequency or the field. It is easier experimentally to vary the field and this is usually the procedure used.

The spectroscopic splitting factor, g, has the value 2.002322 for a free electron. The quantity g is not a constant, but a tensor quantity, whose value depends on the orientation of the molecule containing the unpaired electron with respect to the magnetic field. A value of g averaged over all orientations is obtained for solution, gas phase or powdered samples. In a crystal where movement is restricted the value of g is dependent on the orientation of the crystal. When the paramagnetic species is located in a crystal site of cubic symmetry the g value is independent of orientation and is therefore isotropic. If the paramagnetic species is in a crystal site of lower symmetry the g value is dependent on orientation of the crystal and is therefore anisotropic. For an anisotropic case the g_z value, where z designates as the direction coincident with the highest-fold rotation axis, is equivalent to $g_{||}$, the g value when the axis of highest rotation is parallel to the applied magnetic field. The g_x and g_y values which are equal in a tetragonal site are designated as $g_\perp$, the value of g when the applied magnetic field is perpendicular to the z axis. The angle between the direction of the magnetic field and the z axis is designated as θ. The g value is then calculated by the following equation:(113)

$$g^2 = g_{||}{}^2\cos^2\theta + g_{\perp}{}^2\sin^2\theta. \qquad (33)$$

The ESR spectrum can be presented as a plot of intensity against the applied field but it is customary to present the first derivative of the absorption curve plotted against the strength of the applied magnetic field.

When a lone electron moves in an orbit which includes a nucleus with a nuclear spin, I, there will be an interaction (hyperfine) which will result in the absorption signal being split into 2I+1 components. The case of an electron interacting with a nucleus having a nuclear spin of $\frac{1}{2}$ will be considered as an example. For each value of m_s, $\pm \frac{1}{2}$, the nuclear spin angular momentum quantum number can have values of $\pm \frac{1}{2}$. As a result of this interaction there are four energy levels. The selection rules for ESR permit transitions only when $\Delta m_I = 0$ and $\Delta m_s = \pm 1$. So for the four levels resulting from the interaction two transitions would be allowed resulting in two peaks in the absorption curve. When the spectrum is split by n equivalent nuclei of equal spin, the absorption signal is split into 2nI+1 components.

Electron spin resonance studies are important in the study of uranium(V) coordination compounds because they provide a means of confirming the uranium(V) oxidation state and also give information concerning the bonding in the compounds. Because of the strong tendency of U(V) to disproportionate to U(IV) and U(VI) it is important to establish that U(V) is present in a compound and that disproportionation has not occurred. Since

U(VI) has no unpaired electrons it does not give an ESR signal. U(IV) with two unpaired electrons gives an ESR signal only in unusual circumstances because of the strong spin-spin interaction. An ESR signal for powdered samples obtained at room temperature is therefore considered confirmation of the uranium(V) oxidation state.

The data for the ESR spectra for the compounds prepared in this study are presented in Table II and the ESR spectra are shown in Figures II to IX. The ESR spectra were obtained and the data is given in Table II for three compounds, $UCl_5 \cdot TCAC$, $UCl_5 \cdot SOCl_2$ and Pr_4NUCl_6, previously studied by Selbin, Ortego and Gritzner.[98] The spectra of these three compounds are shown in Figures X to XII. The values obtained for these compounds are of interest for comparison with the values for the new uranium(V) compounds.

The g_{ave} values obtained for $[UCl_4 dipy]Cl$ and $UCl_5 \cdot Ph_3P$, $UCl_5 \cdot diphos$, $[U_2Cl_9Ph_2Bi]Cl$ and $UCl_5 \cdot 2C_9H_7NO$ are very close to the free electron g value, 2.002322. These compounds give very narrow signals ranging in width from 7.2 to 39 gauss. All of these compounds have ligands containing aromatic rings which have empty low energy molecular orbitals into which the one 5f electron might be delocalized.

In contrast to the above situation the compounds which had been studied previously[98], $UCl_5 \cdot TCAC$, $UCl_5 \cdot SOCl_2$ and Pr_4NUCl_6, have g_{ave} values of 1.090, 1.063 and 1.106, which are much lower than the free electron value. These compounds give very broad signals, markedly different from those of the new compounds. It is significant

TABLE II

DATA FOR ELECTRON SPIN RESONANCE SPECTRA[a]

Compound	Gain	Field (Gauss)	Frequency Mc/sec	g_{ave}	Signal Width (Gauss)
$[UCl_4dipy]Cl$	63	3363	9436	2.005	15.0
$UCl_5 \cdot Ph_3P$	45	3360	9442	2.008	25.5
$UCl_5 \cdot diphos$	50	3339	9444	2.022	39
(UCl_5+Ph_3Sb)	360	3260	9447	2.071	>2000
$[U_2Cl_9(Ph_3Bi)]Cl$	220	3365	9442	2.005	7.2
$UCl_4T \cdot 4HT$	710	3372	9339	1.980	>2000
$UCl_5 \cdot 2C_9H_7NO$	200	3372	9442	2.001	15.0
$UCl_5 \cdot 4C_9H_7NO$	63	2953	9443	2.286	1124.0
$UCl_5 \cdot TCAC$	200	6168	9433	1.090	1280.0
Pr_4NUCl_8	120	6202	9439	1.063	1256
$UCl_5 \cdot SOCl_2$	140	6114	9460	1.106	1220

[a]All values given are for powdered samples except for (UCl_5+Ph_3Sb) whose spectrum was obtained in nitromethane solution.

FIGURE II

The ESR spectrum of powdered $[UCl_4dipy]Cl$,

ν = 9436 Mc/s, field strength: 3363 $\pm$ 100 gauss.

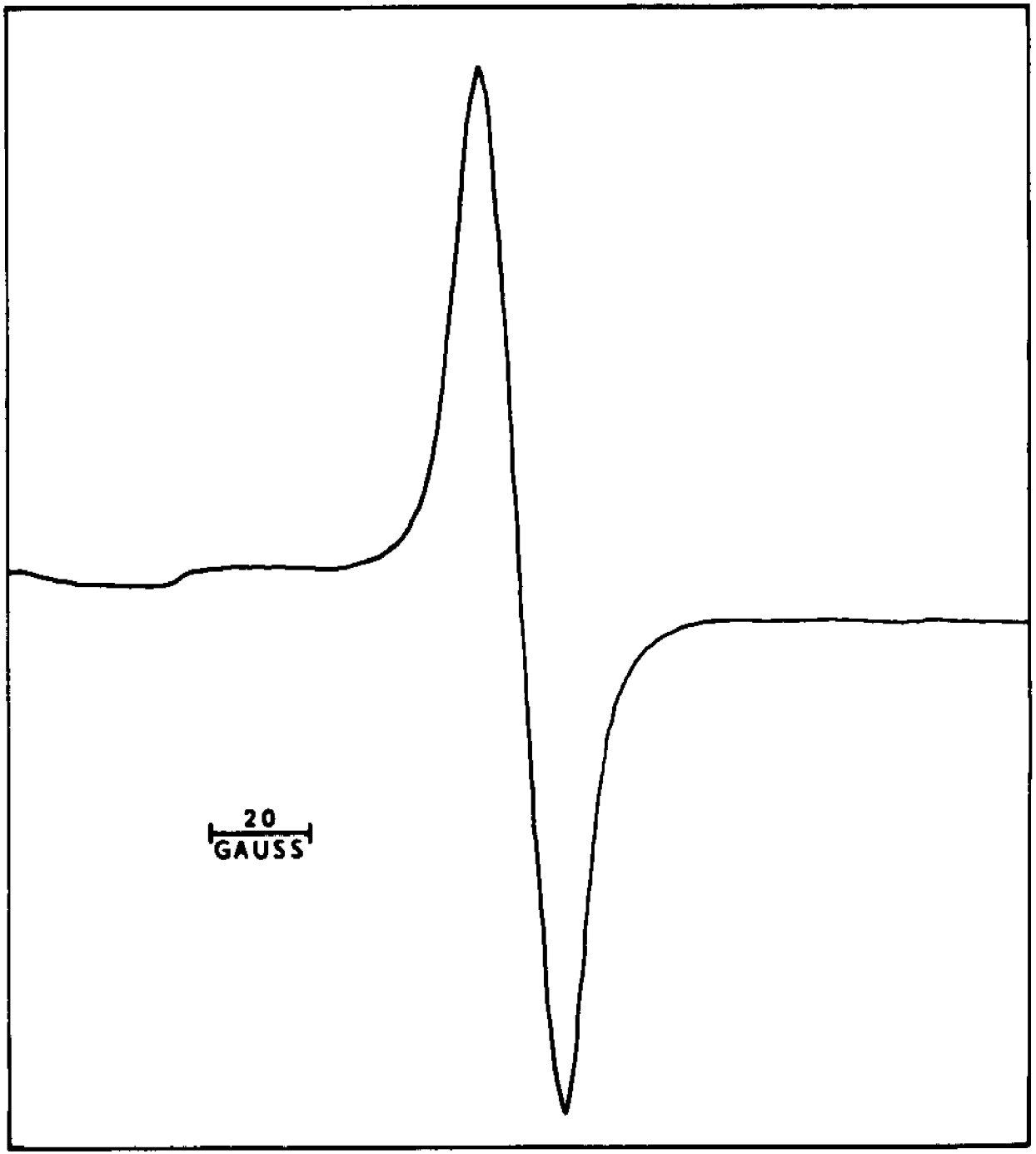

20
GAUSS

FIGURE III

The ESR spectrum of powdered $UCl_5 \cdot Ph_3P$,

ν = 9442 Mc/s, field strength: 3360 $\pm$ 250 gauss.

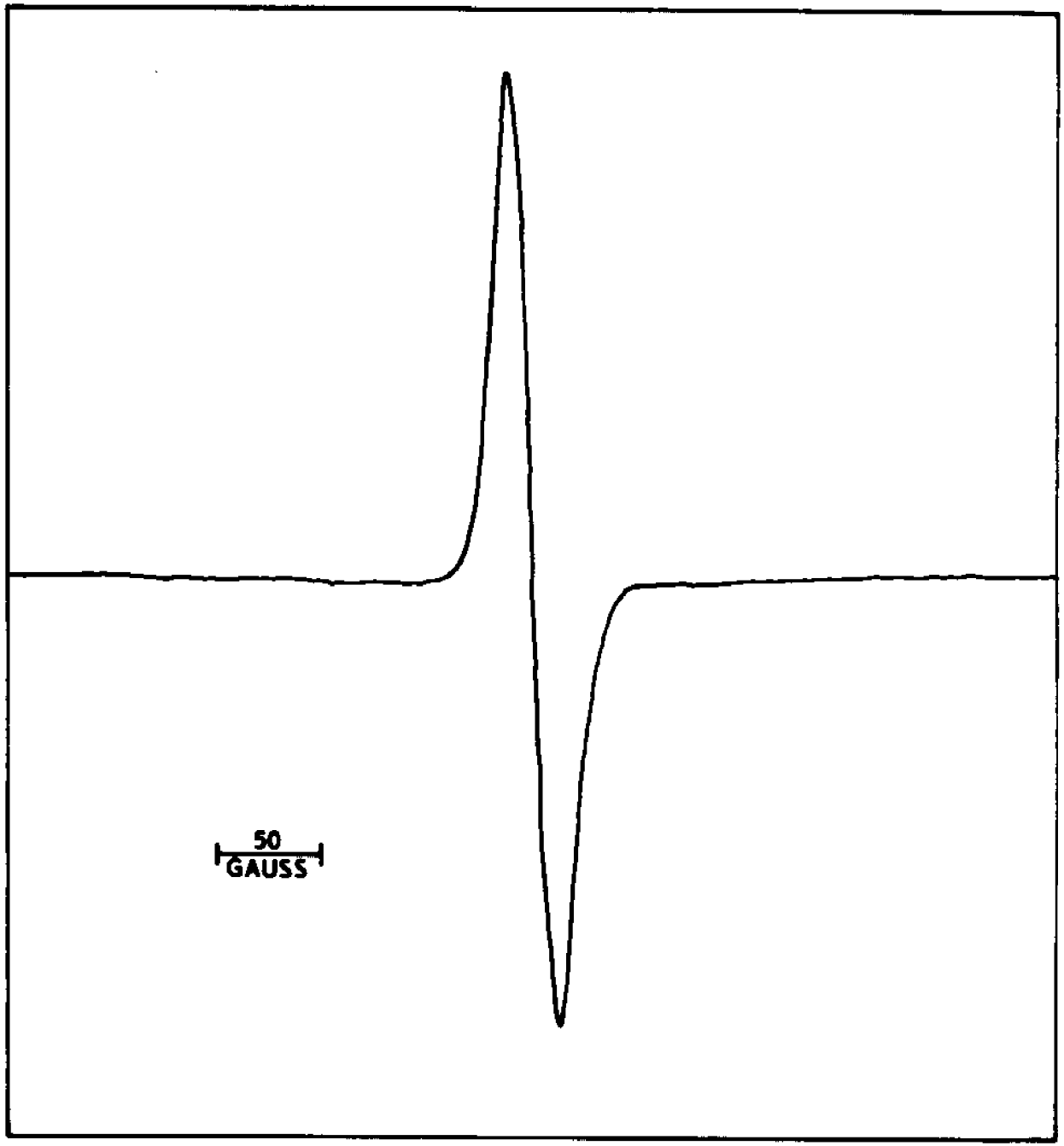

50
GAUSS

FIGURE IV

The ESR spectrum of powdered $UCl_5 \cdot$diphos,

ν = 9444 Mc/s, field strength: 3339 $\pm$ 100 gauss.

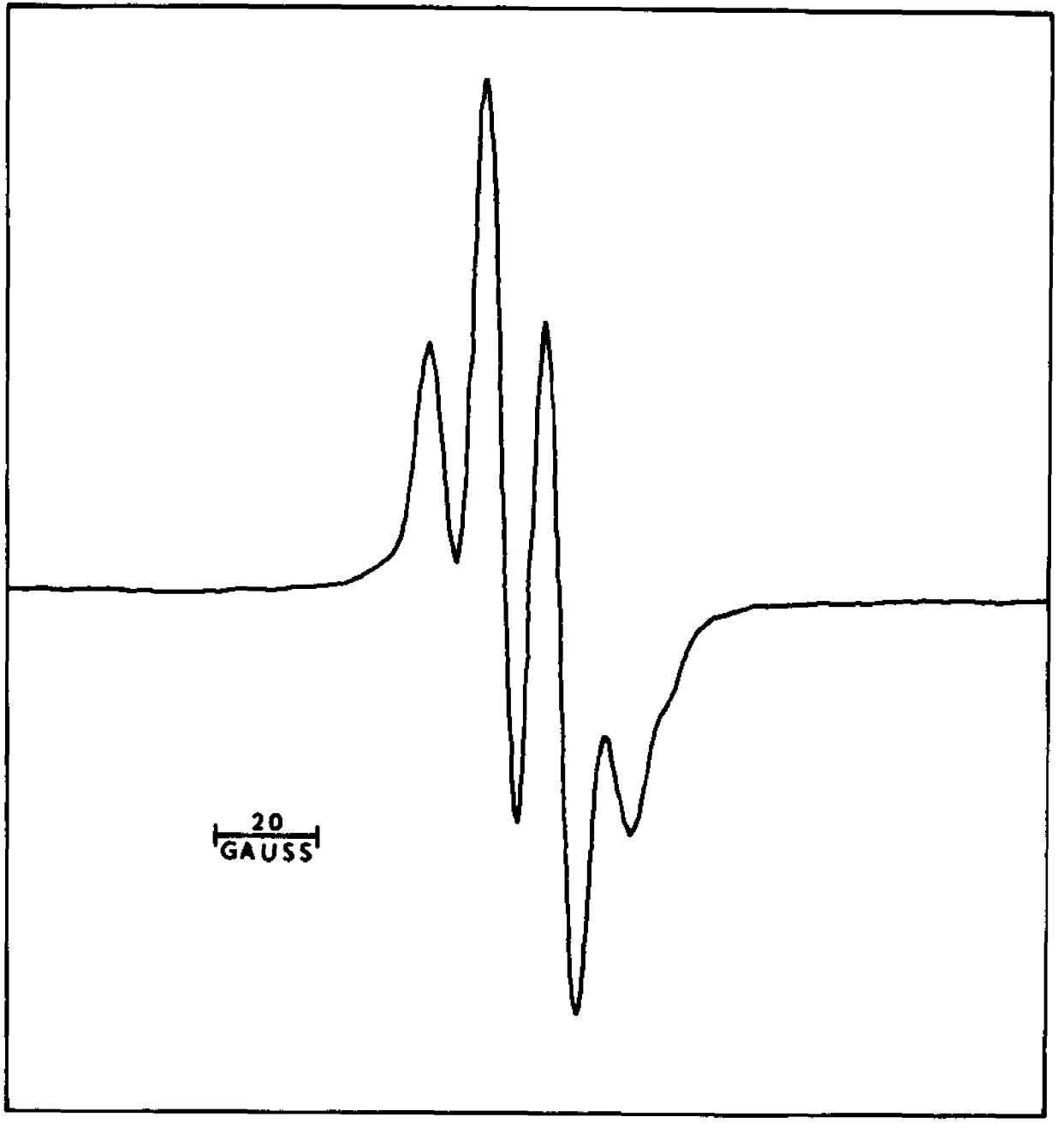

20
GAUSS

FIGURE V

The ESR spectrum of (UCl_5+Ph_3Pb) in nitromethane, ν = 9447 Mc/s, field strength: 3260 $\pm$ 2000 gauss.

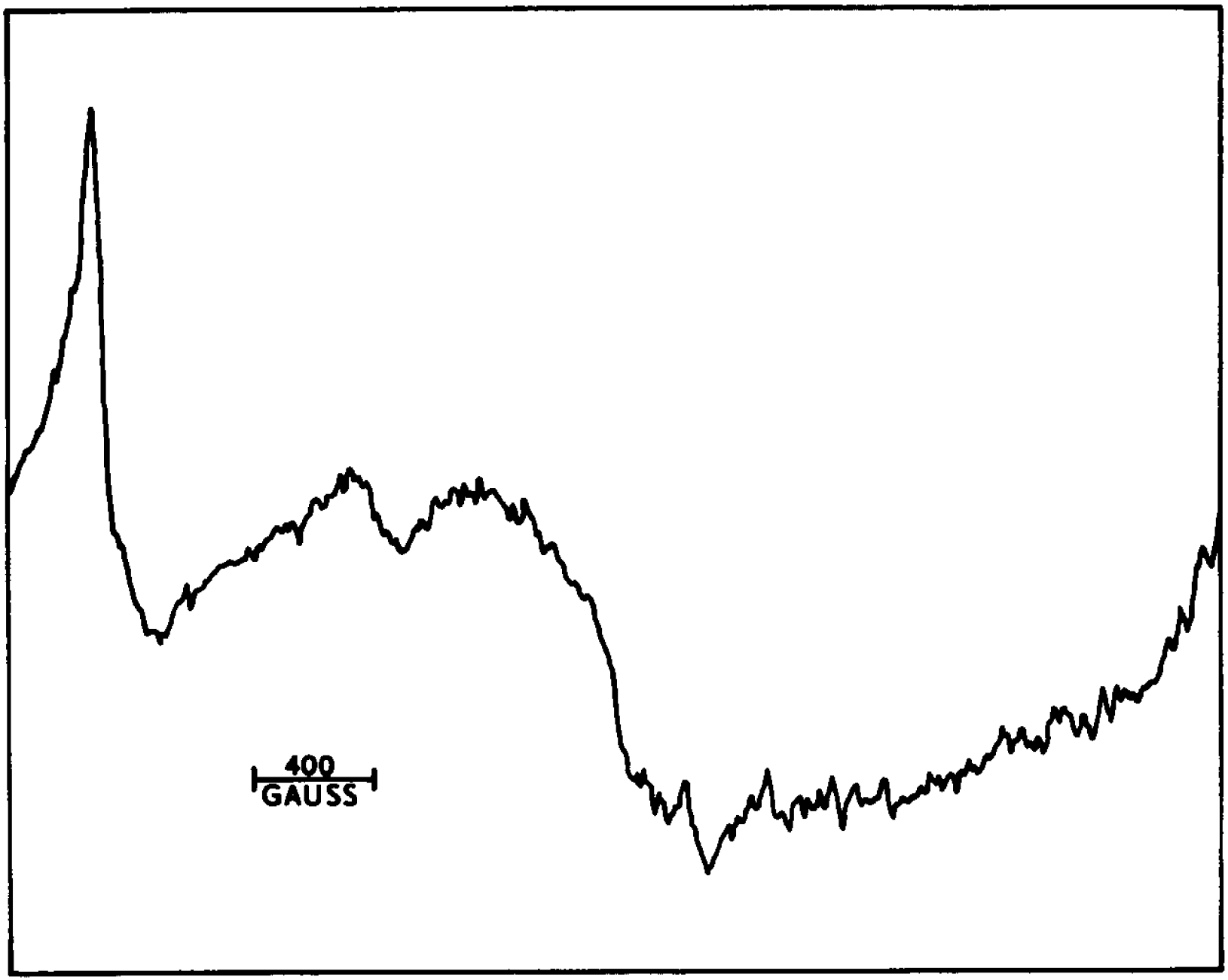

400
GAUSS

FIGURE VI

The ESR spectrum of powdered $[U_2Cl_9(Ph_3Bi)]Cl$

ν = 9442 Mc/s, field strength: 3365 $\pm$ 100 gauss.

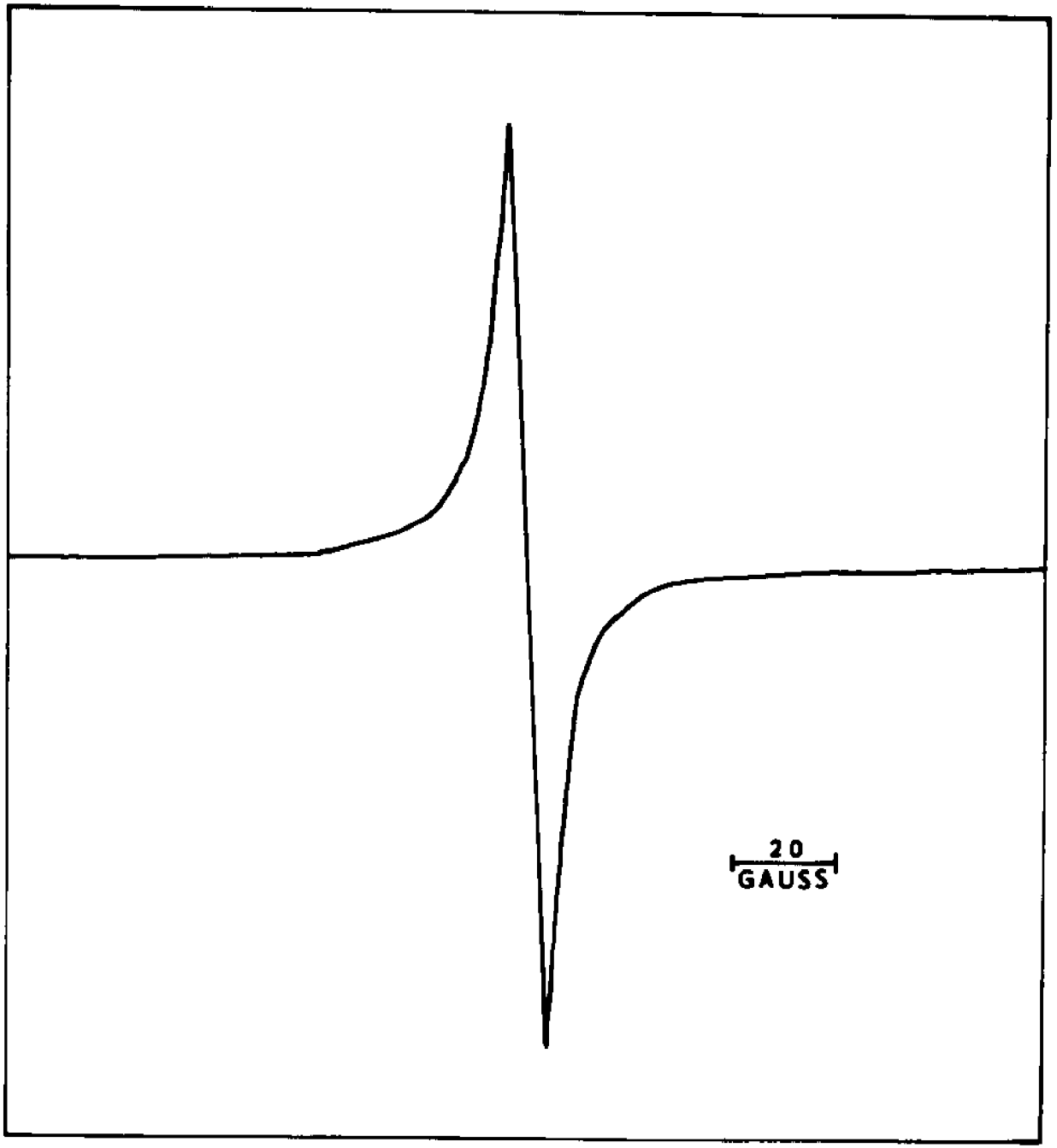

20
GAUSS

FIGURE VII

The ESR spectrum of powdered $UCl_4T \cdot 4HT$,

ν = 9359 Mc/s, field strength: 3372 $\pm$ 2000 gauss.

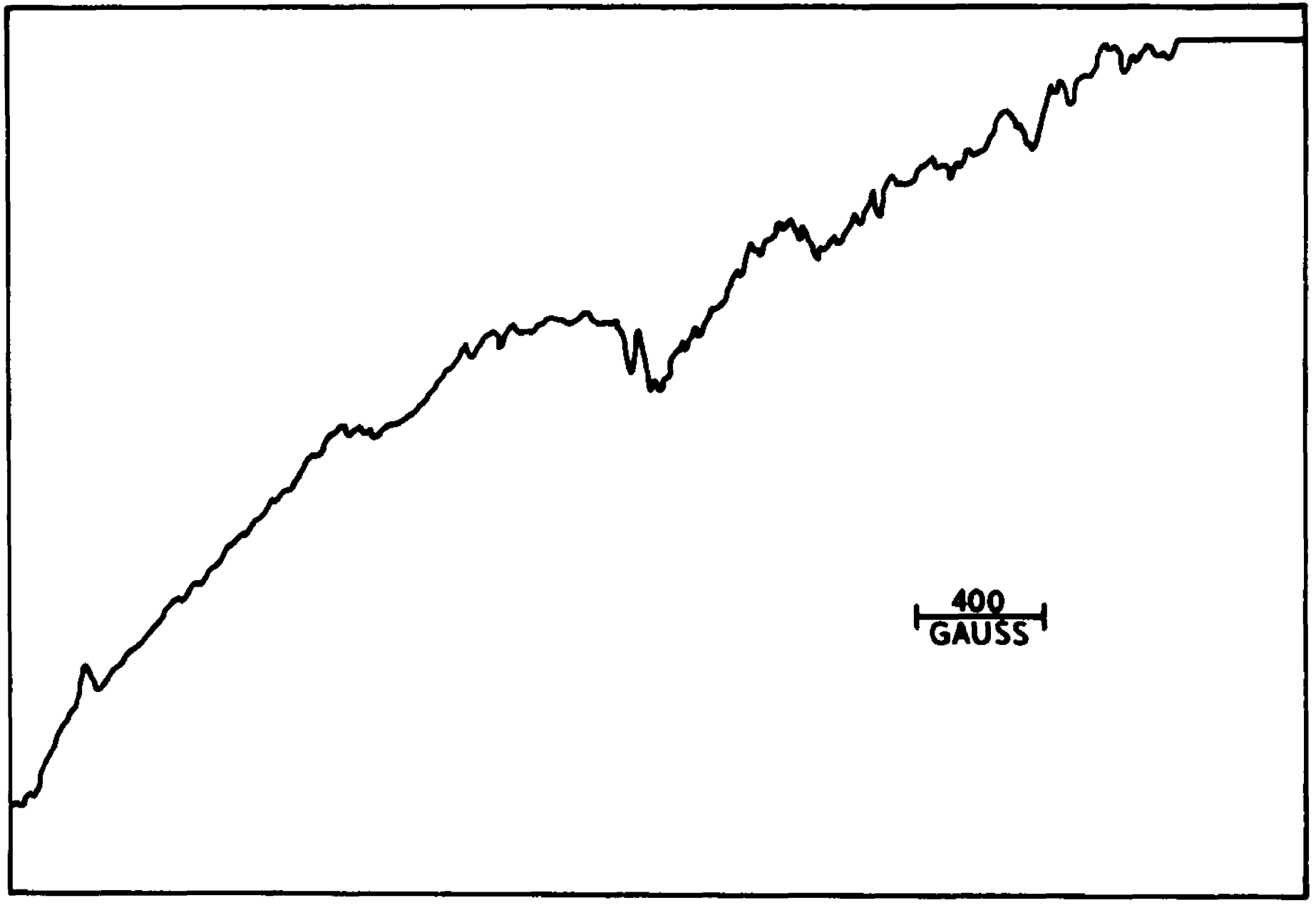

400
GAUSS

FIGURE VIII

The ESR spectrum of powdered $UCl_5 \cdot 4C_9H_7NO$,

ν = 9442 Mc/s, field strength: 3372 $\pm$ 250 gauss.

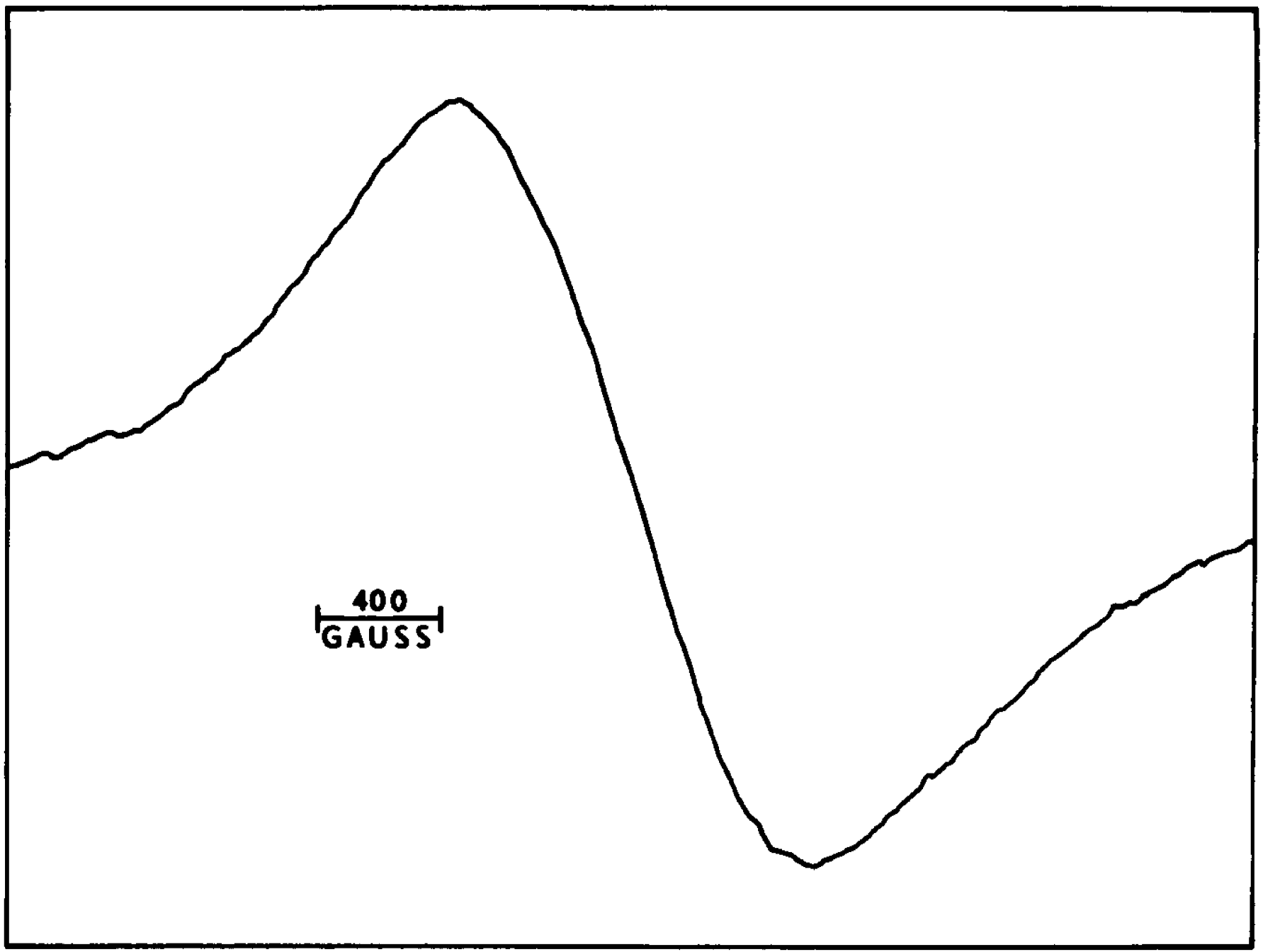

400
GAUSS

FIGURE IX

The ESR spectrum of powdered $UCl_5 \cdot 2C_9H_7NO$,

ν = 9443 Mc/s, field strength: 2953 $\pm$ 2000 gauss.

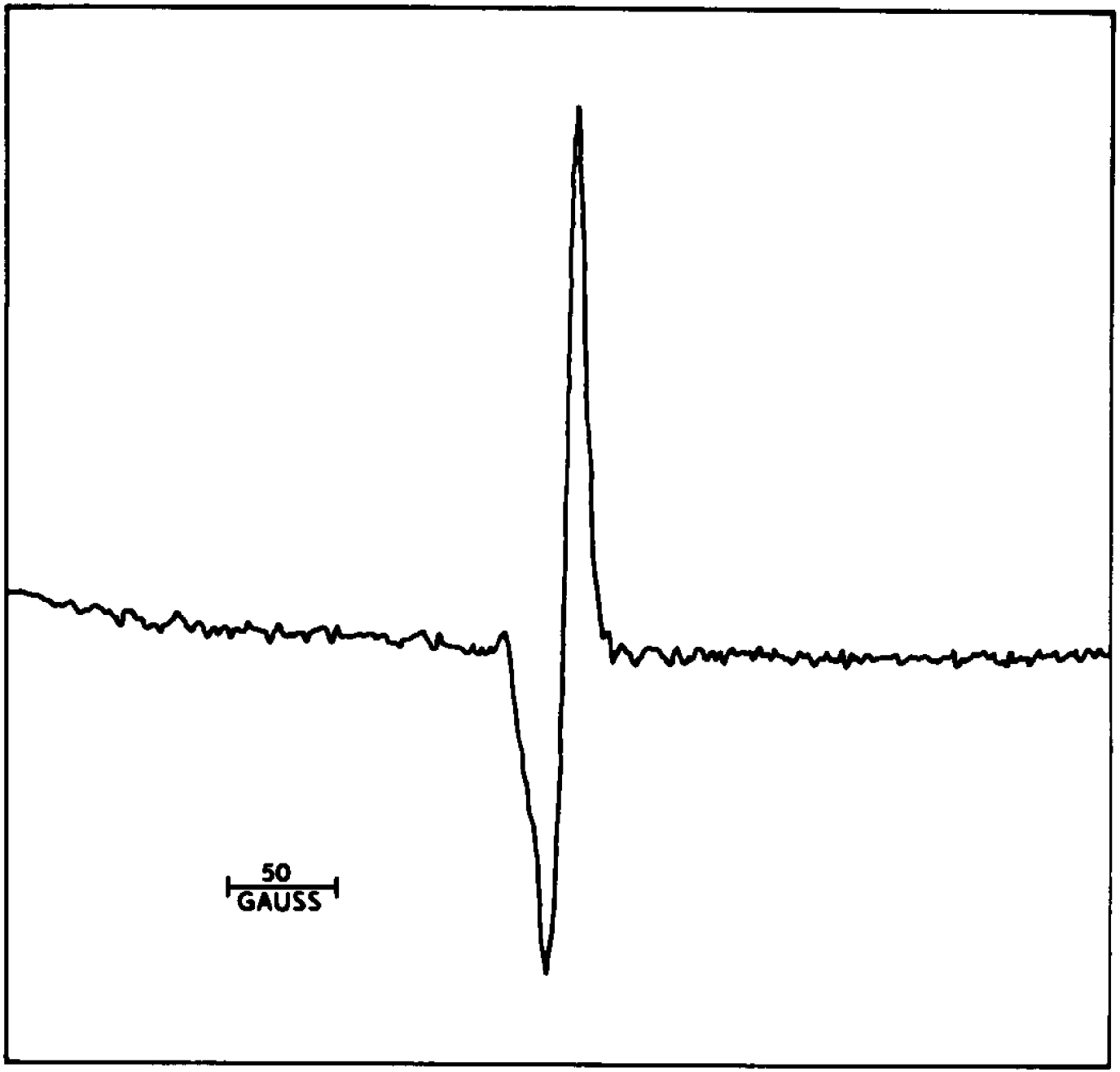

50
GAUSS

FIGURE X

The ESR spectrum of powdered $UCl_5 \cdot TCAC$,

ν = 9433 Mc/s, field strength: 6186 $\pm$ 2000 gauss.

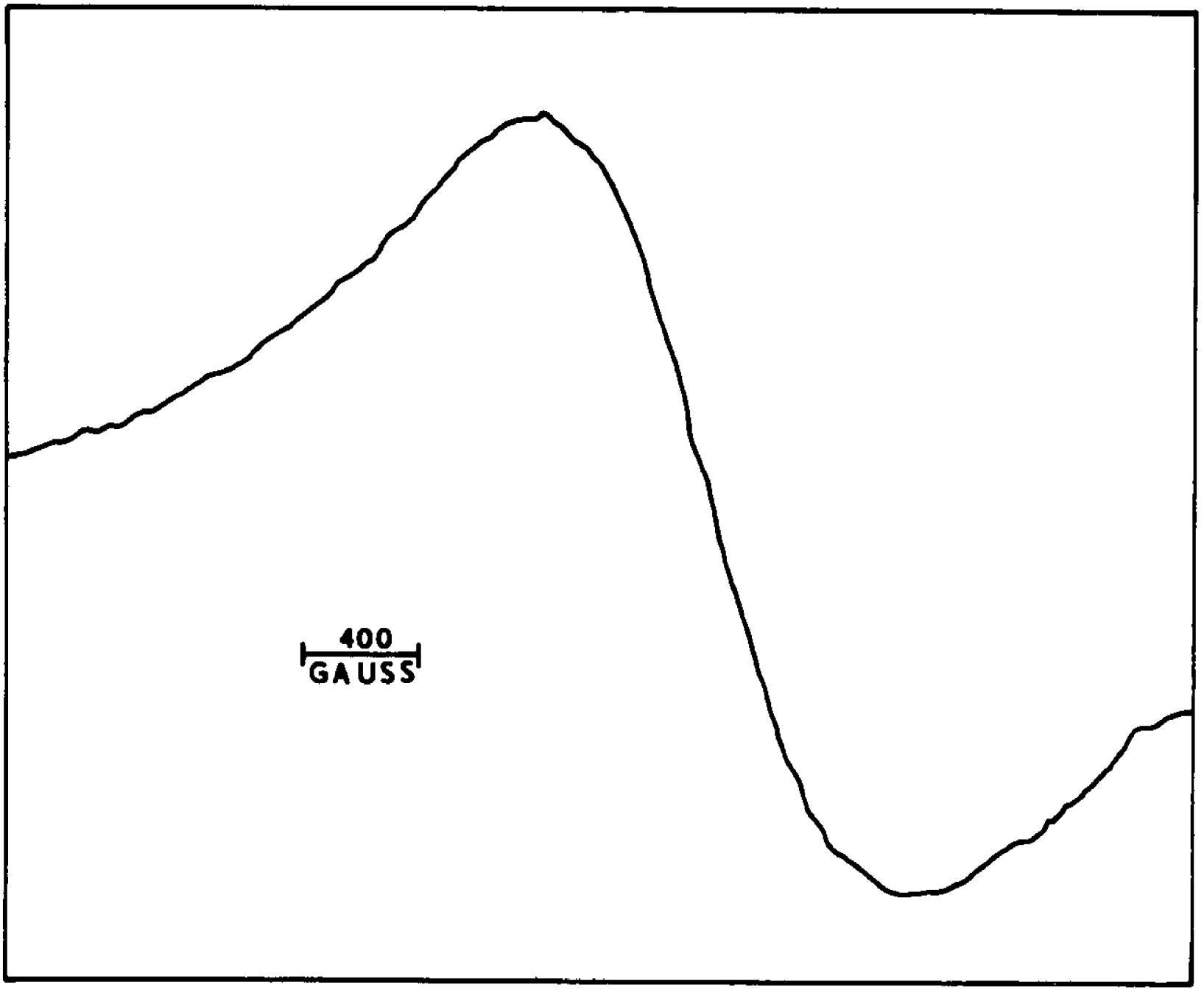

400
GAUSS

FIGURE XI

The ESR spectrum of powdered Pr_4NUCl_6,

ν = 9439 Mc/s, field strength: 6202 $\pm$ 2000 gauss.

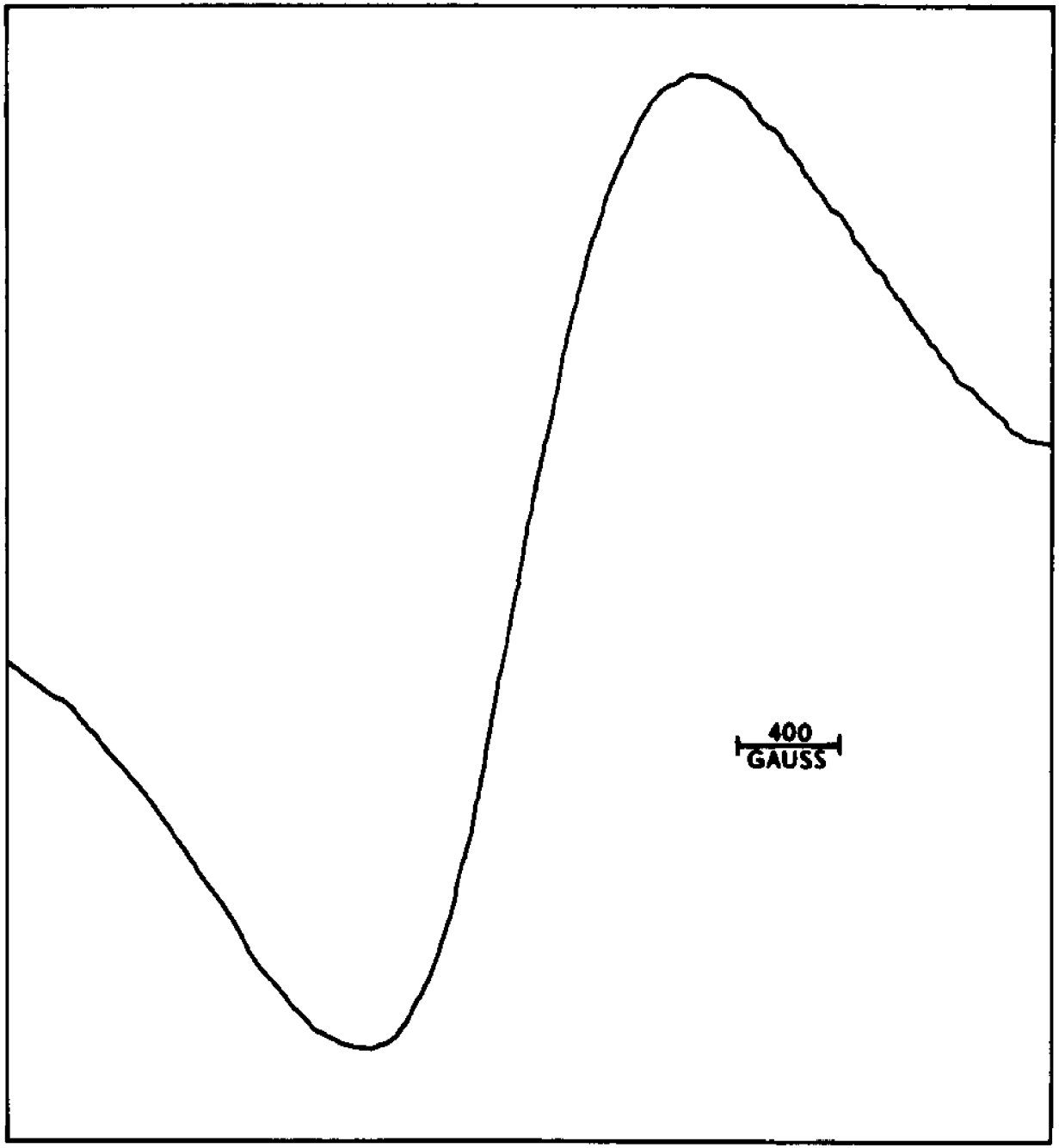
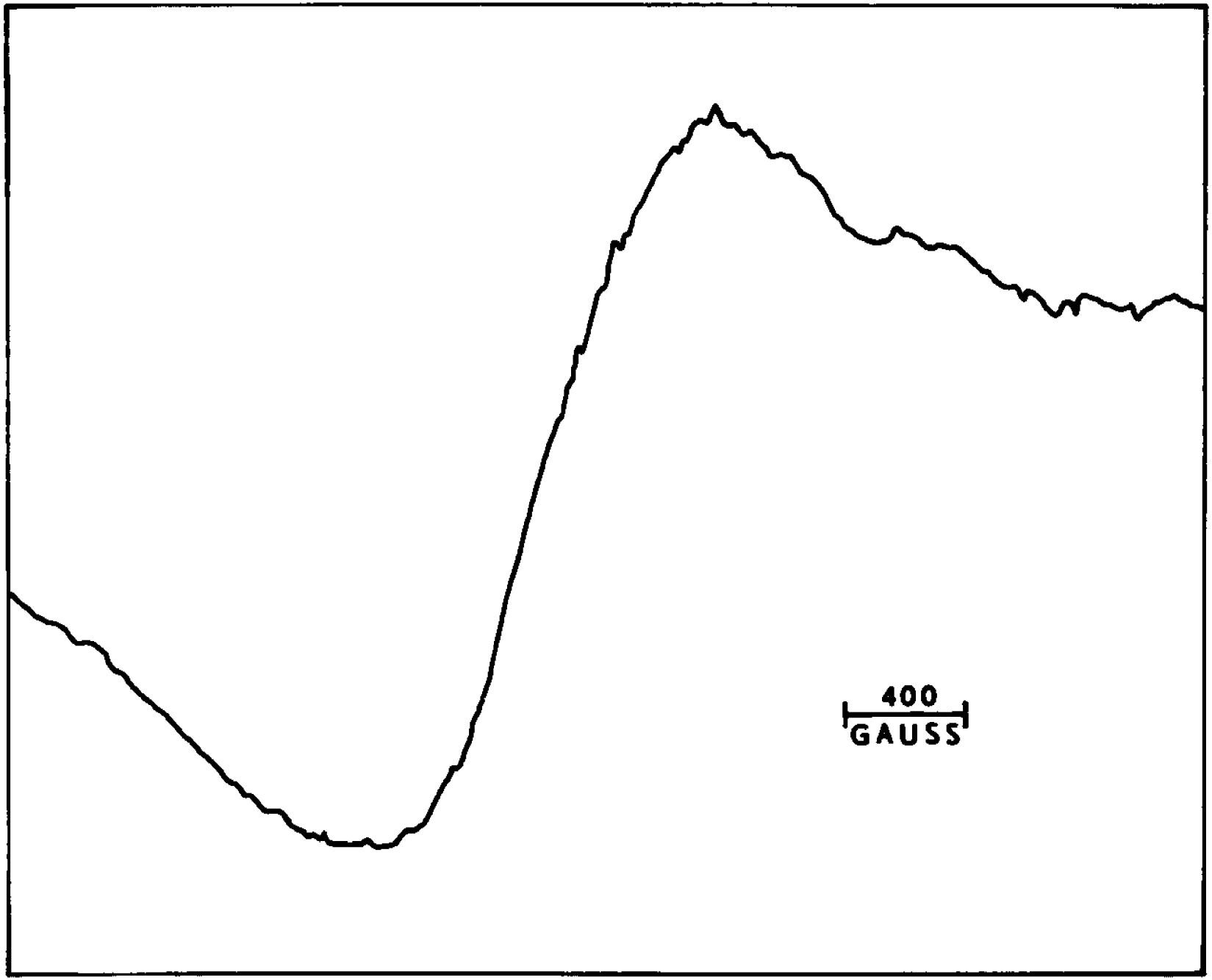

400
GAUSS

FIGURE XII

The ESR spectrum of powdered $UCl_5 \cdot SOCl_2$,

ν = 9460 Mc/s, field strength: 6114 $\pm$ 2000 gauss.


400
GAUSS

that the ligands present in these compounds, which give broad signals and low g_{ave} values, do not have empty low energy molecular orbitals available for delocalization of the 5f electron.

The g_{ave} values close to the free electron value and the narrow signals obtained for $[UCl_4 \cdot dipy]Cl$, $UCl_5 \cdot Ph_3P$, $UCl_5 \cdot diphos$, $[U_2Cl_9(Ph_3Bi)]Cl$ and $UCl_5 \cdot 2C_9H_9NO$ are considered evidence for the delocalization of the uranium(V) 5f electron into the available molecular orbitals of the ligands.

The ESR spectrum obtained for the compound formed by reaction of $UCl_5 \cdot TCAC$ and Ph_3Sb is for a nitromethane solution and, as seen in Figure V, it is very different from the spectra obtained for the other compounds. Because this compound was not obtained in pure form and was not characterized, it is not possible to explain this spectra other than to note that splitting might be expected in this case because ^{121}Sb (natural abundance 57.25%) has a nuclear spin of 5/2 and ^{123}Sb (natural abundance 42.75) has a nuclear spin of 7/2.

The ESR spectrum of $UCl_5 \cdot 4C_9H_7NO$, Figure VIII, is unusual for the compounds prepared in this study because it gives a broad signal even though the four 9-hydroxyquinoline molecules present do contain aromatic rings and delocalization of the electron might be expected. However, the g_{ave} value, 2.286, is appreciably higher then that obtained for any of the other compounds. As discussed above this compound has a higher magnetic moment, $\mu_{eff} = 2.84$BM, than found for the other compounds. This high magnetic moment and the high coordination number are apparently consistent with the unusual ESR spectrum.

The broad, weak ESR signal shown in Figure VI for $UCl_4T \cdot 4HT$ is apparently related to the high coordination number and dysymmetry of this compound. The g_{ave} value, 1.980, is lower than for the other compounds and is not close to the free electron g value. This indicates less electron delocalization for this apparently 10-coordinate complex.

The only compound prepared which did not give an ESR signal was $[U_2Cl_9(Ph_3As)]Cl$. The absence of a signal for this compound is probably due to the presence of two 5f electrons in the system. Assuming that the uranium(V) ions are joined by chloride bridging they might be close enough for spin-spin interaction to occur between the two f electrons and prevent observation of electron spin resonance.

The ESR spectrum of $UCl_5 \cdot$diphos, Figure IV, is the only spectrum obtained of a powdered sample which shows splitting. The nuclear spin of ^{31}P is $\frac{1}{2}$ and two phosphorous atoms are present in the molecule. In general, when the spectrum is split by n equivalent nuclei of equal spin, the number of lines is $2nI+1$. Thus, for $UCl_5 \cdot$diphos the absorption spectrum would be expected to be split into 3 lines. This is observed in the ESR spectrum of $UCl_5 \cdot$diphos. The ESR spectrum of $UCl_5 \cdot Ph_3P$, the other compound containing phosphorous, does not show any splitting. Comparing the structure of triphenylphosphine and ethylenebis(diphenylphosphine) it would seem that the presence of three aromatic rings attached to the phosphorous in triphenylphosphine would make possible greater delocalization of the 5f electron in the aromatic system than would

occur in diphos with but two aromatic rings attached to each phosphorous. If greater delocalization of the 5f electron into the aromatic rings occurs and there is little possibility of interaction with the phosphorous nucleus in the triphenylphosphine then splitting would not be expected in the absorption spectrum of $UCl_5 \cdot Ph_3P$. The narrower signal width for $UCl_5 \cdot Ph_3P$, 25.5 gauss compared with 39 gauss for UCl_5·diphos, and the g_{ave} value of 2.008 for $UCl_5 \cdot Ph_3P$ which is closer to the free electron value, 2.002322, than the UCl_5·diphos value of 2.022, both suggest that there is greater delocalization of the electron in $UCl_5 \cdot Ph_3P$ than is found in UCl_5·diphos.

C. Vibrational Spectra

The absorption bands from the infrared spectra recorded from 600 to 4000 cm^{-1} for the compounds prepared in this study and for the corresponding ligands are presented in Tables III, IV and V. The spectra confirm the presence of the ligands in all the new compounds prepared. The infrared spectra confirm that the very stable UO_2^{++} ion is not present in these compounds. As mentioned previously the ease with which uranium(V) oxidizes and forms the UO_2^{++} ion makes it necessary to establish that this ion is absent in the compounds. The presence of UO_2^{++} is revealed by a strong, somewhat broad band in the 920 - 940 cm^{-1} region and a less intense band in the 830 - 860 cm^{-1} region, the asymmetric and symmetric O-U-O stretching frequencies, respectively. Bands do not occur in these regions in any of the complexes except $[UCl_4dipy]Cl$ and $UCl_5.2C_9H_7NO$. The bands observed in $[UCl_4dipy]Cl$ at 938 cm^{-1} and 917 cm^{-1} appear to be the result of a shifting and splitting of a band

TABLE III

INFRARED ABSORPTION BANDS (cm^{-1}) OF URANIUM(V) COMPOUNDS AND LIGANDS, NaCl REGION[a]

$[UCl_4dipy]Cl$	dipy	$UCl_5 \cdot Ph_3P$	Ph_3P	$UCl_5 \cdot$diphos	diphos
			3060 w		
3226 w	3400 m	2930 x	2930 x	2930 x	2930 x
3615 w	3100 w	2860 x	2860 x	2860 x	2858 x
3090 x					
2950 x	2800 w	1583 m	1583 m	2405 m	2370 m
		1473 x	1475 x	1590 m	1585 w
2735 w		1463 s	1467 s	1465 x	1463 x
1608 s	1625 s		1436 s	1443 s	1434 s
1577 m		1440 s		1378 s	1377 s
1532 m	1550 m		1432 s	1315 w	1306 w
1475 x		1377 s	1377	1190 w	1190 w
1440 w	1440 s	(1367)	(1366)	1178 w	1160 w
1380 x	1410 s	1337 w	1326 w	1130 m	1097 m
1321 w		1315 w	1308 w	1115 m	1080 m
1287 m			1280 w	1067 m	1067 m
1240 w	1240 s	1268 w	1270 w	1027 w	1024 m
1174 m		1187 w	1177 w	997 m	997 m
1162 w	1135 m	1162 m	1155 w	955 w	
1108 w		1119 s	1090 s		845 w
1092 w	1084 s	1057 w			752 m
1077 m	1082 s	1023 w	1072 m		740 m
1045 w		995 s	1025 s	743 s	
1038 w	1055 m	948 m	995 m	733 s	727 s
1015 s	1035 s	867 m	917 w		704 w
1008 w	1010 w	788 w	854 w	692 s	692 s
938 s	983 s		754 w	665 w	677 w
917 s		747 s	748 s		
822 w		728 s	743 s		
805 w	885 m		723 w		
798 w		687 s	697 s		
762 s	758 s	608 m	608 m		
738 m	735 m				
662 m					

[a] Bands marked with an x are Nujol bands.

TABLE IV

INFRARED ABSORPTION BANDS (cm^{-1}) OF URANIUM COMPOUNDS AND LIGANDS, NaCl REGION[a]

$[U_2Cl_9(Ph_3As)]Cl$	Ph_3As	UCl_5+Ph_3Sb	Ph_3Sb	$[U_2Cl_9(Ph_3Bi)]Cl$	Ph_3Bi
3450 w	3450 m	3400 m	3040 m	3400 m	
3000 s	3000 s	2930 x	2935 x	(3045)	
2935 x					
2860 x	2290 m	2870 x	2870 x	2935 x	2940 x
	1960 w		2340 w	2860 x	2868 x
	1880 w		1950 w	2722 w	2730 w
	1820 w		1880 w	(2664)	
1668 w	1750 w	1800 w	1830 w	1593 m	1507 m
				1566 m	
1604 w		1608 m	1575 m		
1578 w	1575 m		1540 w	1462 x	1464 x
(1490)	1490 s	1460 x	1460 x	1437 s	(1459)
1463 x			1430 s		1432 w
1444 x	1430 s	1380 s	1380 s		1427 m
1397 m			1320 w		
(1370)	1390 w		1300 w	1376 s	1378 s
1317 w	1310 s	1260 m	1250 w	(1365)	(1366)
1264 m	1275 w	1210 w	1200 w	1327 w	1326 w
			1190 w		
1187 w	1185 w	1160 w	1170 w	1307 w	1300 w
1167 w	1155 m		1130 m	1260 m	1260 w
		1150 w			
	(1085)	1090 w	1095 w	1187 w	1184 w
1078 s	1075 s	1075 w	1075 w	1162 w	1155 w
	(1065)	1030 w			1062 m
			972 m	1075 m	1056 m
1023 w	1022 s	950 m			
997 s	1000 s	935 m	950 w	1012 m	1015 m
	990 w		878 m	992 s	997 m
958 w	977 w	844 m	860 m	983 w	
	912 m	800 m		964 w	
	853 w			918 w	
754 m	845 w	730 m	730 s	812 m	847 m
743 s	736 s	685 m	695 s		(737)
725 w				727 w	726 s
687 s	695 s			685 m	697 s

[a]Bands marked with x are due to Nujol.

TABLE V

INFRARED ABSORPTION BANDS (cm^{-1}) OF URANIUM COMPOUNDS AND LIGANDS, NaCl REGION[a]

$UCl_5 \cdot 2C_9H_7NO$	C_9H_7NO	$UCl_5 \cdot 4C_9H_7NO$	$UCl_4T \cdot 4HT$	HT
		3425 w		
		3175 w		
(3200)	3425 w	(3090)		3200 w
(3120)		(3075)	2930 s	2925 s
(3022)		(3040)	2860 s	2866 s
2904 x	2960 x	2930 x	2368 w	
2860 s	2900 s	2860 s		
		(2742)		
2740 w	2735 w	(2720)	1585 s	1614 m
2580 w	2680 w	2660 w	1543 w	
2320 w	2375 w	2577 w	1523 s	1557 m
	1948 w			1508 w
	1908 w		1495 w	(1490)
	1895 w		1462 s	1463 s
	1825 w			1455 s
	1732 w			(1425)
	1705 w		1416 s	
1630 s	1627 w	1652 s	1375 s	1378 s
1590 s	1595 m	1592 s	1362 s	
	1583 s	1585 m		
1554 s		1550 s	1322 s	
(1542)			1290 s	
1497 m	1508 s	1497 m	1259 m	1267 s
1468 x	1464 x	1457 x	1242 w	1250 s
1457 s				
1420 s	1413 s	1418 s	1227 w	
1385 s	1380 s	1377 s	1213 s	1211 m
1304 s		1302 s	1187 w	1170 w
1295 s	1280 s		1073 w	
			1060 w	1050 m
1270 s	1268 s	1270 s	1045 w	
1226 s	1226 s	1223 s		982 w
1207 w	1205 s	1197 m	964 m	955 m
1177 m	1165 s	1175 m	947 w	
				920 m
1145 m	1140 m	1138 m	913 w	
1105 s	1095 m	1105 s	874 s	875 m
		1095 m	832 w	
1062 m	1060 m	1057 m		

Table V cont.

$UCl_5 \cdot 2C_9H_7NO$	C_9H_7NO	$UCl_5 \cdot 4C_9H_7NO$	$UCl_4T \cdot 4HT$	HT
				789 w
1045 m	(1045)	(1045)	740 m	742 m
1032 w	1028 w	1032 w		
987 w		985 w	728 m	
943 s	975 s		713 m	718 m
		910 s		
902 s	897 s	900 s		
890 m	(894)	885 m	687 w	677 w
	867 m			(668)
822 s	820 s	818 s		
802 m	(804)	800 m		
(775)	788 w	(773)		
762 s	782 s	762 s		
		(750)		
738 s	745 s	735 s		
715 w	712 s			
687 m	640 m			
623 m		625 m		

[a]Bands marked with x are due to Nujol.

which occurs at 983 cm^{-1} in the free ligand. There is no band present in the complex at 983 cm^{-1}. In $UCl_5 \cdot 2C_9H_7NO$ the band at 923 appears to result from a ligand band which has shifted from 975 cm^{-1}.

The compound $UCl_5 \cdot Ph_3PO$ has been prepared and studied by Bagnall, Brown and DuPreez.(88) To establish clearly that $UCl_5 \cdot Ph_3P$ is a new compound and does not contain phosphine oxide the infrared spectrum of $UCl_5 \cdot Ph_3P$ was examined to determine whether a band corresponding to the P=O vibrational frequency is present. In Ph_3PO the P=O band is found at 1192 cm^{-1} and on forming $UCl_5 \cdot Ph_3PO$ the band is shifted to 973 cm^{-1}.(88) Other workers report that on complexation the P=O band is shifted to the 1063 - 1093 cm^{-1} region.(116) $UCl_5 \cdot Ph_3P$ does not show any strong bands in these regions which are not already present in the free ligand. The infrared spectrum of $UCl_5 \cdot$diphos also rules out the possibility of this compound containing the oxide of the ligand. The infrared spectra of these compounds containing phosphorous donor ligands have also been examined for possible P-H bands. The absence of bands in the region of 2430 cm^{-1} where P-H bands are usually observed(117) is confirmation that these compounds do not exist as phosphonium salts. However, evidence for the existence of the U-P bond has been obtained from infrared data and will be presented below.

The infrared spectrum of $[U_2Cl_9(Ph_3As)]Cl$ has been checked to verify that this compound does not contain the arsine oxide. The As=O band which occurs at 880 cm^{-1} in the free Ph_3AsO ligand is reported to be shifted to a lower frequency by about 40 cm^{-1} when a complex is formed.(118) No band is found at this frequency in $[U_2Cl_9(Ph_3As)]Cl$.

The infrared spectrum of six compounds has been studied in the cesium iodide region (700 - 200 cm^{-1}). This region is of interest because frequencies for U-O, U-N, U-P and U-Cl bonds may be expected in this region. The infrared spectra of $[UCl_4dipy]Cl$, $UCl_5 \cdot 4C_9H_7NO$, $UCl_4T \cdot HT$, $UCl_5 \cdot Ph_3P$, $UCl_5 \cdot$diphos, $[U_2Cl_9(Ph_3As)]Cl$ and the corresponding ligands are shown in Figures XIII to XVII. The absorption bands for these spectra are given in Tables VI and VII.

It has been possible to assign the frequencies for the U-Cl bonds in the compounds $UCl_5 \cdot Ph_3P$, $UCl_5 \cdot$diphos, $[UCl_4dipy]Cl$ and $[U_2Cl_9(Ph_3As)]Cl$. In $[UCl_4dipy]Cl$ the three bands at 327, 315 and 310 cm^{-1} are all assigned as U-Cl frequencies. The three bands at 325, 318 and 310 cm^{-1} in $UCl_5 \cdot Ph_3P$ are assigned as U-Cl frequencies. In $UCl_5 \cdot$diphos bands at 330 and 318 cm^{-1} are assigned as U-Cl frequencies. A third band at about 307 - 309 may contain an additional U-Cl frequency but this is covered by a ligand band.

In $[U_2Cl_9(Ph_3As)]Cl$ the band at 305 cm^{-1} is assigned as a U-Cl frequency. It is possible that two additional bands may also be U-Cl frequencies. The shape of the band envelope indicates that the bands which occur in the ligand at 319, 328, 335 and 340 cm^{-1} may have shifted to a higher energy in the complex. The bands at 360, 368 and 374 cm^{-1} in $[U_2Cl_5(Ph_3As)]Cl$ may well represent the shifted bands. If this band shift has occurred then additional assignments for U-Cl frequencies could be made at 317 and 328 cm^{-1}.

Assignments have previously been made for U-Cl frequencies. Bagnall and coworkers(81) have reported values which range from

FIGURE XIII

a. Infrared Spectrum of $[UCl_4dipy]Cl$ from 200 to 700 cm^{-1} in Nujol Mull.

b. Infrared Spectrum of dipy from 200 to 700 cm^{-1} in Nujol Mull.

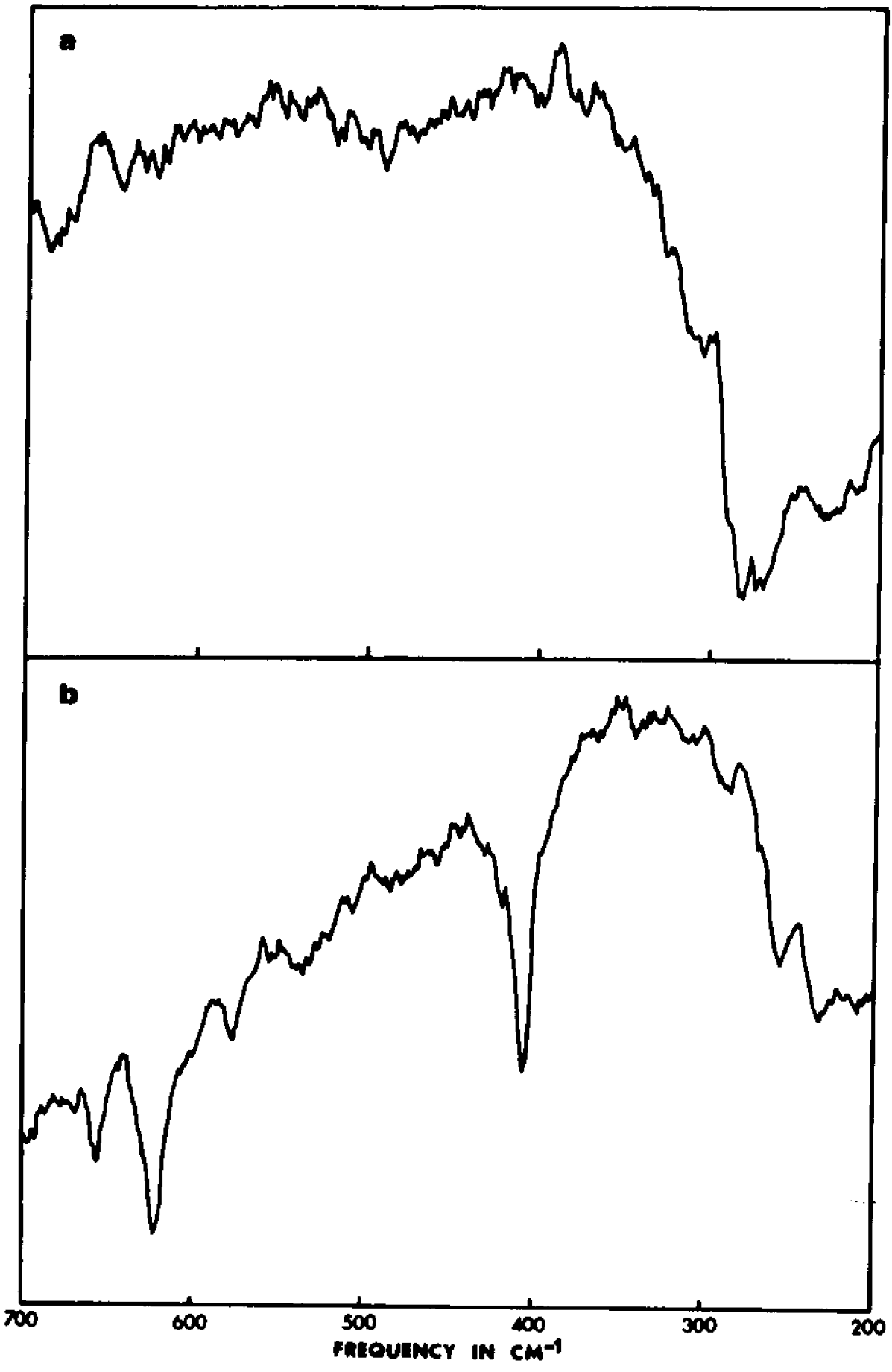

a
b
700
600
500
400
300
200
FREQUENCY IN CM⁻¹

FIGURE XIV

a. Infrared Spectrum of $[U_2Cl_9(Ph_3As)]Cl$ from 200 to 700 cm^{-1} in Nujol Mull.

b. Infrared Spectrum of Ph_3As from 200 to 700 cm^{-1} in Nujol Mull.

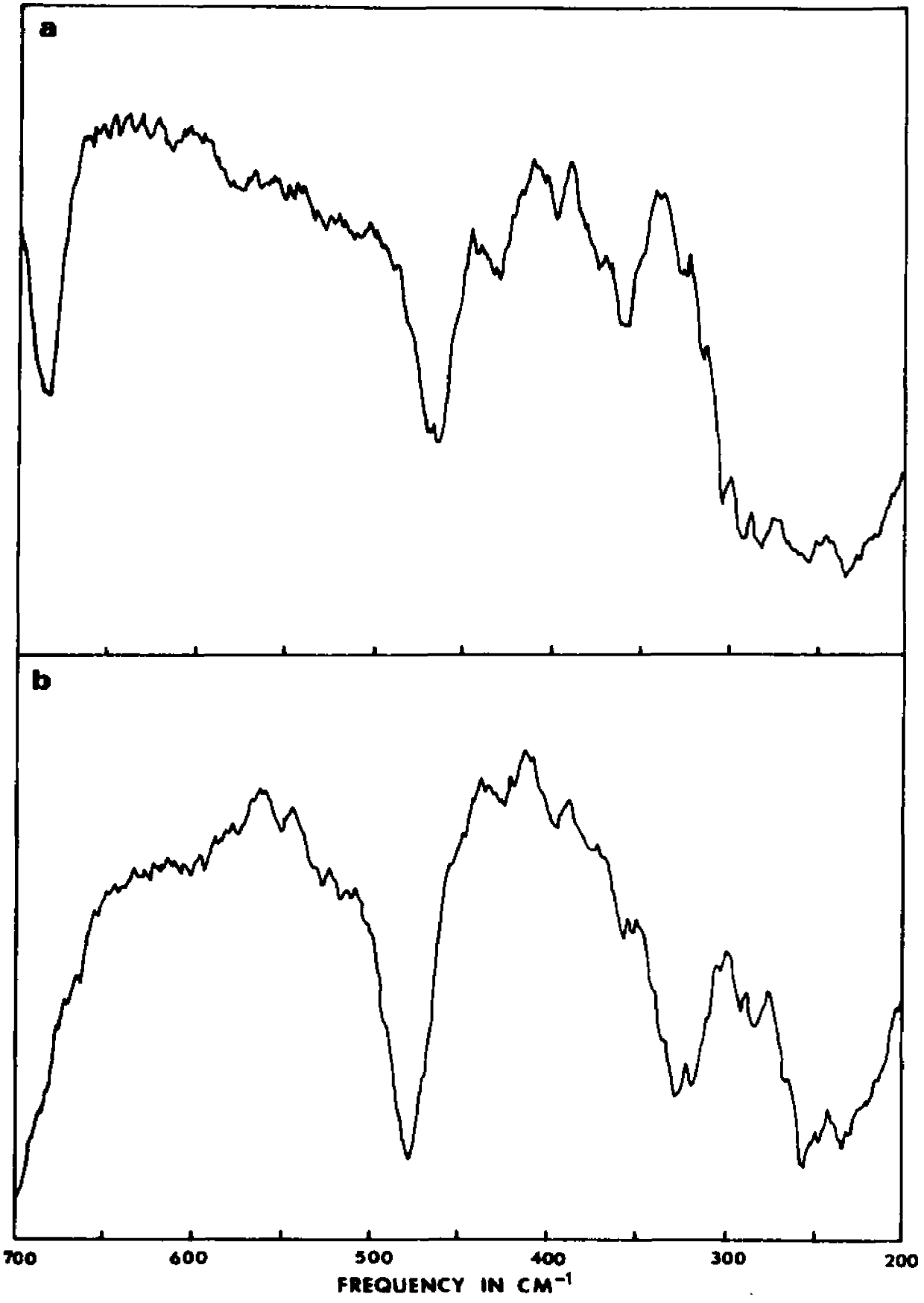

a
b
700
600
500
400
300
200
FREQUENCY IN CM^{-1}

FIGURE XV

a. Infrared Spectrum of $UCl_5 \cdot Ph_3P$ from 200 to 700 cm^{-1} in Nujol Mull.

b. Infrared Spectrum of Ph_3P from 200 to 700 cm^{-1} in Nujol Mull.

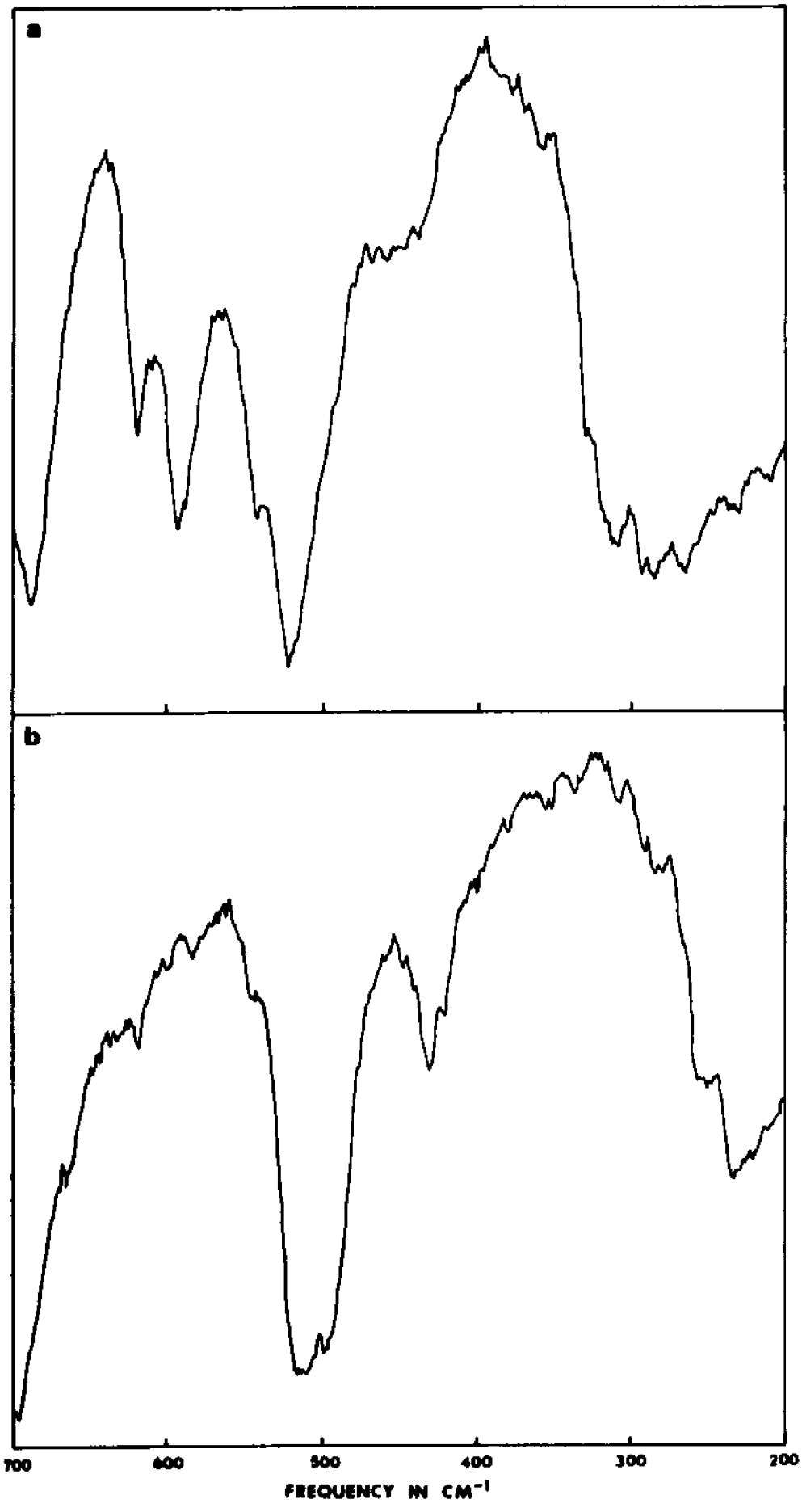

a
b
700
600
500
400
300
200
FREQUENCY IN CM⁻¹

FIGURE XVI

a. Infrared Spectrum of UCl_5·diphos from 200 to 700 cm^{-1} in Nujol Mull.

b. Infrared Spectrum of diphos from 200 to 700 cm^{-1} in Nujol Mull.

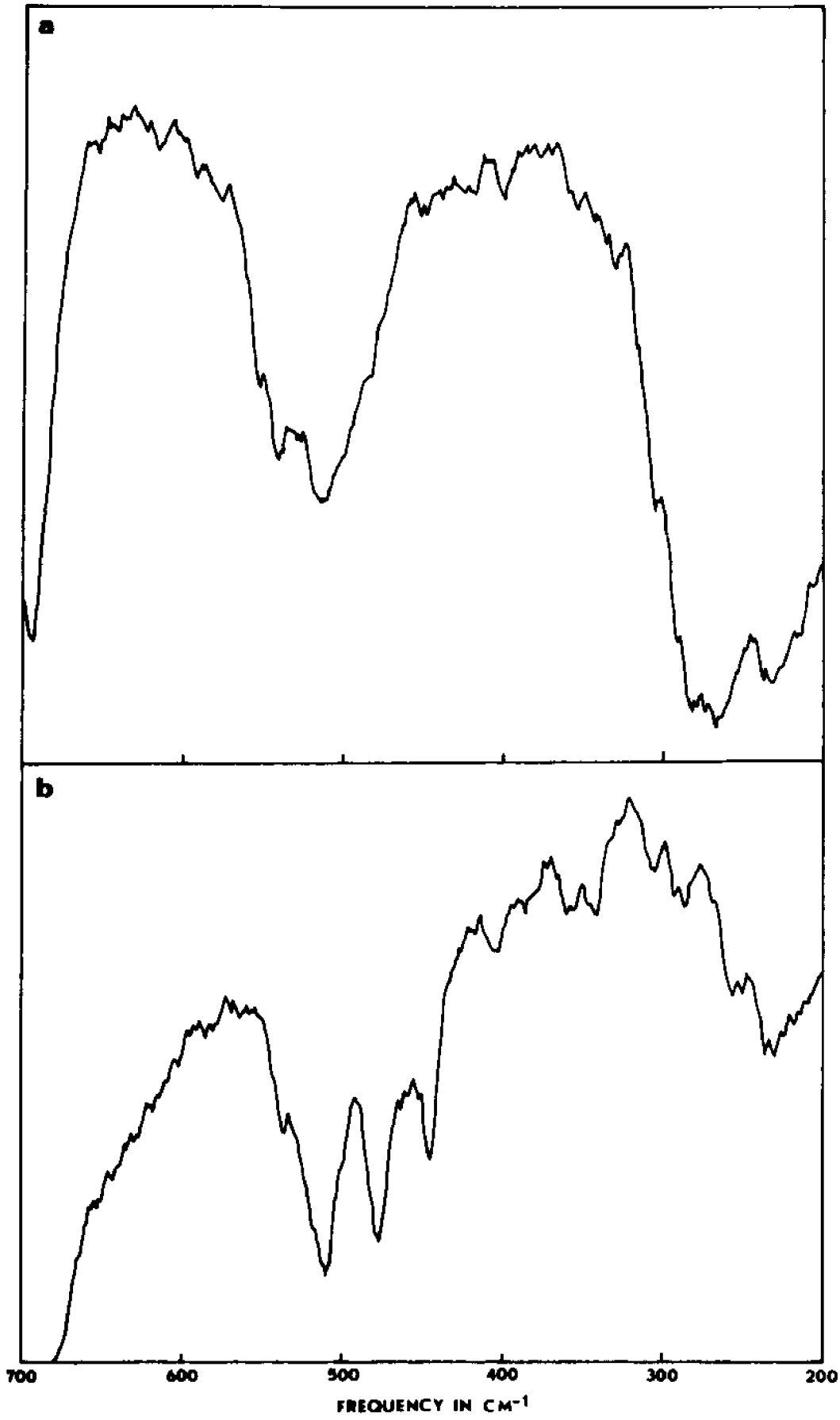

a
b
700
600
500
400
300
200
FREQUENCY IN CM-1

FIGURE XVII

a. Infrared Spectrum of $UCl_4 \cdot 4HT$ from 300 to 600 cm^{-1} in Nujol Mull.

b. Infrared Spectrum of HT from 300 to 600 cm^{-1} in Nujol Mull.

c. Infrared Spectrum of $UCl_5 \cdot 4C_9H_7NO$ from 300 to 600 cm^{-1} in Nujol Mull.

d. Infrared Spectrum of C_9H_7NO from 300 to 600 cm^{-1} in Nujol Mull.

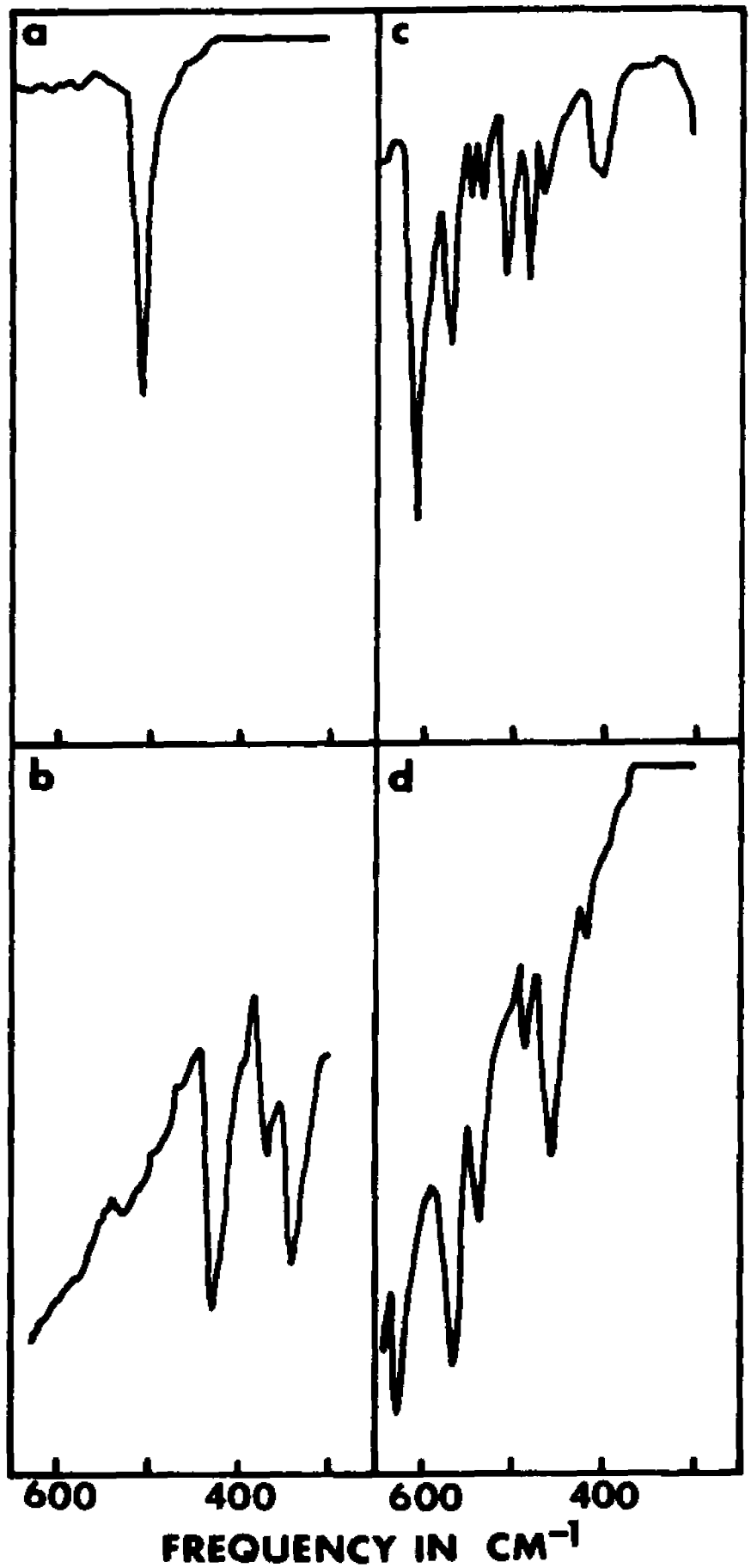

a
c
b
d
600
400
600
400
FREQUENCY IN CM⁻¹

TABLE VI

INFRARED ABSORPTION BANDS (cm^{-1}) OF URANIUM(V) COMPOUNDS AND LIGANDS, CsI REGION

$UCl_5 \cdot Ph_3P$	Ph_3P	Assignments	$UCl_5 \cdot$diphos	diphos	Assignments	$[U_2Cl_9(Ph_3As)]Cl$	Ph_3As	Assignments
690 s	692 s		696 s				694 s	
620 m	620 m		617 m	537 m		686 s		
592 s	600 w		594 s	512 s			605 w	
(587)	582 w		(578)			584 w	594 w	
	562 w		(533)			575 w	575 w	
542 m	542 m		540 m			552 w	550 w	
521 s	515 s		523 s	446 s		534 w	534 w	
	507 s		(503)			523 w	528 w	
468 m			482 w			516 w	518 w	
439 w	439 m		452 w			507 w		
437 w			448 w			(488)		
433 w	430 w		421 w	407 w		467 s	468 s	
358 w	357 w		400 w	400 w		438 w	(443)	
338 w	338 w		380 w	385 w		430 m	(432)	
330 m	330 w		354 w	354 w		382 m	382 w	
325 m		U-Cl	342 w	346 w		374 m	374 m	
318 s		U-Cl	338 w	340 m		368 m	358 m	
310 s		U-Cl	330 w		U-Cl	360 m		
304 s	306 w		318 w		U-Cl	328 m	328 s	
292 s	291 s		307 m	307 m		317 m	319 m	
286 s	285 s		292 w	292 w		305 s		U-Cl
(268)	(268)		282 s	286 s		292 s	292 m	
265 s		U-P	273 s		U-P	282 s	284 m	
255 m	255 m		268 s	267 s		265 s	267 w	

Table VI cont.

$UCl_5 \cdot Ph_3P$	Ph_3P	Assignments	$UCl_5 \cdot$diphos	diphos	Assignments	$[U_2Cl_3(Ph_3As)]Cl$	Ph_3As	Assignments
247 m	247 m		265 s			256 s	256 m	
233 m	231 m			256 m		244 s	245 m	
211 m	214 m		245 m	249 m		233 s	231 m	
			238 m	235 m		215 s	222 m	
			232 m	225 m		208 m	208 w	
			215 m	219 m				
				208 m				

TABLE VII

INFRARED ABSORPTION BANDS (cm^{-1}) OF URANIUM(V) COMPOUNDS AND LIGANDS, CsI REGION

$[UCl_4 dipy]Cl$	dipy	Assignments	$UCl_5 \cdot C_9H_7NO$	C_9H_7NO	Assignments	$UCl_4 \cdot HT$	HT	Assignments
687 s	694 m		635 s	628 s		542 w		
682 m	655 s		568 m	568 m			525 m	
	(632)		543 m			505 s		U-O?
645 m	623 s			530 s		(Broad)		
580 w	570 w		530 m				428 s	
525 w	538 w		507 m		U-N		370 m	
519 w	520 w		482 m	482 m			340 s	
503 w	506 w		468 w	460 s				
492 m		U-N		418 m				
445 w	445 w		400 m		U-O			
	408 w		(broad)					
	406 s							
342 w	342 w							
335 m	335 m							
327 m		U-Cl						
315 m		U-Cl						
310 m		U-Cl						
305 m	307 m							
300 m								
287 s	292 s							
282 s	282 s							
273 s	276 s							
260 s	264 s							
233 s	232 s							
226 s	225 s							
213 s	211 s							

303 cm^{-1} to 310 cm^{-1} for 3 hexachlorouranium(V) compound and 1 octachlorouranium(V) compound. They also reported a value of 285 cm^{-1} for $UCl_5 \cdot Ph_3PO$ and 304 cm^{-1} for $UCl_5 \cdot (C_8H_{17})_3PO$.(81) The U-Cl frequency has been assigned as 320 cm^{-1} in UCl_5·TCAC and 315 cm^{-1} in Pr_4NUCl_6.(98)

It is seen in Tables VI and VII that assignments of the U-Cl frequencies in these new compounds are in good agreement with assignments previously made. The presence of more than one U-Cl frequency indicates that the uranium-chlorine bonds are not all equivalent. This would confirm statements made earlier that the compounds have C_{4v} or lower symmetry.

The U-P frequencies have been assigned for $UCl_5 \cdot Ph_3P$ and UCl_5·diphos. In $UCl_5 \cdot Ph_3P$ the U-P frequency is at 265 cm^{-1} and in UCl_5·diphos the U-P frequency is at 272 cm^{-1}. These assignments give direct evidence for the existence of the U-P band. Since no assignments have previously been made for U-P bands no values are available for comparison.

The assignment of the U-N frequency has been made for $[UCl_4dipy]Cl$ and $UCl_5 \cdot 4C_9H_7NO$. In $[UCl_4dipy]Cl$ the band at 492 cm^{-1} is assigned as the U-N frequency and in $UCl_5 \cdot 4C_9H_7NO$ the band at 507 cm^{-1} is given this assignment. These assignments can be compared with other metal-nitrogen bond frequencies. Powell and Shephard(119) report the M-N stretching frequency as 502 cm^{-1} in $[Co(NH_3)_6]Cl_3$, 493 cm^{-1} in $[Co(NH_3)_5Cl]Cl_2$, 498 cm^{-1} in $Pd(NH_3)_4Cl_2 \cdot H_2O$ and 511 cm^{-1} in $[Pt(NH_3)_4]Cl_2$.

In $UCl_5 \cdot 4C_3H_7NO$ it is expected that the U-O bond formed will be a rather weak bond because it must be presumed that the H of the OH group is still bonded to the oxygen. A band at 400 cm^{-1} is assigned as the U-O frequency for this compound. In $UCl_4 \cdot T \cdot 4HT$ it would be expected that the U-O bond would be a stronger bond. Only one strong band and one very weak band are found for this complex between 600 and 300 cm^{-1}. It appears that there has been a shifting of the ligand bands so that the frequencies overlap in the strong broad band centered at 505 cm^{-1}. The U-O frequency is also considered to be included in this band at 505 cm^{-1}. The U-O frequency in $UCl_5 \cdot TCAC$ has been tentatively assigned as 450 cm^{-1}.(98) It would therefore seem reasonable that in $UCl_4T \cdot 4HT$ the U-O frequency would be at 505 cm^{-1}.

D. Electronic Spectra

The electronic absorption spectra of the inner-transition elements, the lanthanides and actinides, are the result of absorption of energy during f-f transitions. The spectra of these elements present quite a contrast to the electronic spectra observed for the transition elements which result from d-d transitions. The electronic absorption spectra of the transition elements are composed of broad bands whereas the spectra obtained for the lanthanides and actinides exhibit very sharp, narrow absorption bands. The difference in the spectra obtained is the result of more efficient shielding of the f electrons by the s and p electrons of the next outer shell. As a result of the more efficient shielding of the f orbitals they are less

perturbed by external fields and the splitting of the energy levels is of small magnitude compared to that observed for the d electron levels. A difference in the shielding of the 4f and 5f levels is responsible for a difference in the intensity of the spectra for the lanthanides and actinides. Because the 5f orbitals have greater spatial extension relative to the 6s and 6p orbitals than the 4f orbitals relative to the 5s and 5p, the 5f orbitals are more affected by ligand fields. Thus it is found that generally the intensity of absorption bands for 5f electron transitions is about ten times greater than that observed for 4f electron transitions. Also the bands of 5f transitions are generally somewhat broader than those for 4f transitions.

The f-f transitions are La Porte forbidden but due to various mechanisms which result from external fields and configuration interactions the transitions do occur. The $5f^1$ electronic configuration generates only the $^2F_{5/2,7/2}$ term level which is split by spin-orbit coupling into two levels. The $^2F_{5/2}$ state with the lower J value will be the lower energy level and $^2F_{7/2}$ will be the excited state. A single transition $^2F_{7/2} \leftarrow {}^2F_{5/2}$ would be predicted for the case of a field free ion 5f electron. The presence of a crystal field will cause further splitting of the eight-fold degenerate $^2F_{7/2}$ and six-fold degenerate $^2F_{5/2}$ levels. Spin-orbit coupling, crystal field and electron-electron repulsion effects are of approximately the same order of magnitude in actinide ions. For the f^1 system only the two factors, spin-orbit coupling and crystal field interactions, will be effective.

The electronic spectra of a few compounds of Pa(IV) and Np(VI), which are isoelectronic with U(V) but are much more stable, have been observed and interpreted.(100, 101, 120-123)

McClynn and Smith(124) have calculated the $^2F_{7/2} \leftarrow {}^2F_{5/2}$ transition in UO_2^+ to be at 6752 cm^{-1}, and this agrees with observed transitions obtained after their calculations had been reported.

The spectra of some U(V) compounds have been studied and the band assignments have been made.(5, 50, 98, 104-106) The theory which has been developed in these studies of $5f^1$ systems is reviewed below. The splitting of the degenerate $^2F_{5/2}$ and $^2F_{7/2}$ levels which will occur in an octahedral field can be determined by the use of group theory. The "double group" representation O_h' for octahedral symmetry is required because J is half-integral for the two states of the $5f^1$ system. The characters of the new operations are obtained for the reducible representations $\Gamma_{5/2}$ and $\Gamma_{7/2}$. The irreducible representations which belong to these reducible representations are then determined. The irreducible states will be the levels which will result from the splitting of both $^2F_{5/2}$ and $^2F_{7/2}$ in a field of octahedral symmetry. The levels obtained are

$$\Gamma_{5/2} \rightarrow \Gamma_7 + \Gamma_8$$

$$\Gamma_{7/2} \rightarrow \Gamma_6 + \Gamma_7' + \Gamma_8'$$

The ordering of the resulting levels has been obtained by solving the appropriate wave functions. Calculations by Goodman(121) for

the Np(VI) $5f^1$ system yielded the relative ordering of the energy levels which is shown in Figure XVIII.

A diagram which shows the effects of a crystal field on the free $5f^1$ ion was prepared by Goodman(121) and is reproduced in Figure XIX. The diagram shows the effect on the energy levels of going from a free ion (no field) in which j-j coupling is more appropriate to a strong field where L-s coupling is operative. The relative arrangement of the energy levels for 5f electrons will generally be as indicated for the intermediate coupling case.

As a result of the splitting of the levels as shown above, four transitions would be possible for the 5f electron of U(V) in O_h symmetry. The four transitions expected are as follows: $\Gamma_7 \rightarrow \Gamma_8$, $\Gamma_7 \rightarrow \Gamma_7'$, $\Gamma_7 \rightarrow \Gamma_8'$ and $\Gamma_7 \rightarrow \Gamma_6$. Experimental observation of U(V) spectra show not 4 bands but rather four groups of bands. The splitting of the four bands has been explained as arising mainly from vibronic transitions.

A uranium(V) molecule which has octahedral symmetry will have the following normal modes of vibration: infrared active, $2T_{1u}$ (ν_3 and ν_4); Raman active, A_{1g} (ν_1), E_{1g} (ν_2), T_{2g} (ν_5); inactive, T_{2u} (ν_6).

Theoretical predictions which will be of importance in consideration of the spectra of U(V) compounds have been summarized (98) from the work of various authors.(5, 123, 125)

The doublet levels (Γ_7, Γ_7', Γ_6), which arise from Kramer's degeneracy, are predicted to be stabilized by spin-orbit coupling and not affected by Jahn-Teller distortations.

FICURE XVIII

Energy Level Diagram of $5f^1$ System

in O_h Symmetry

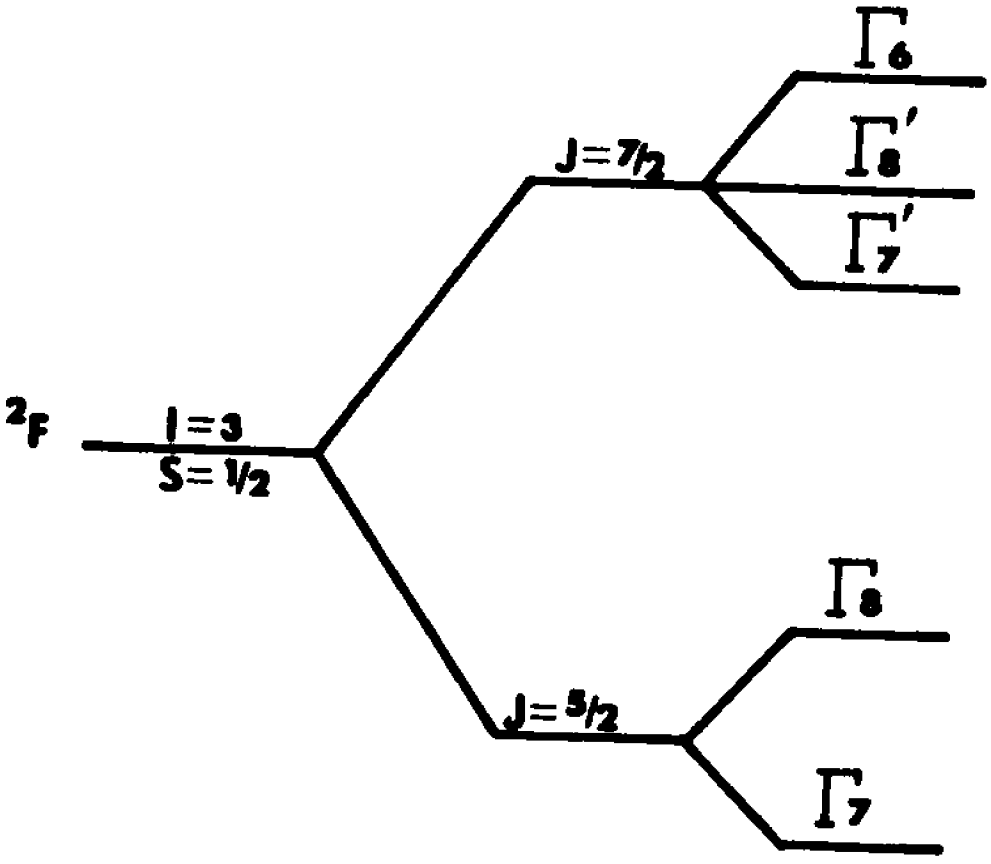
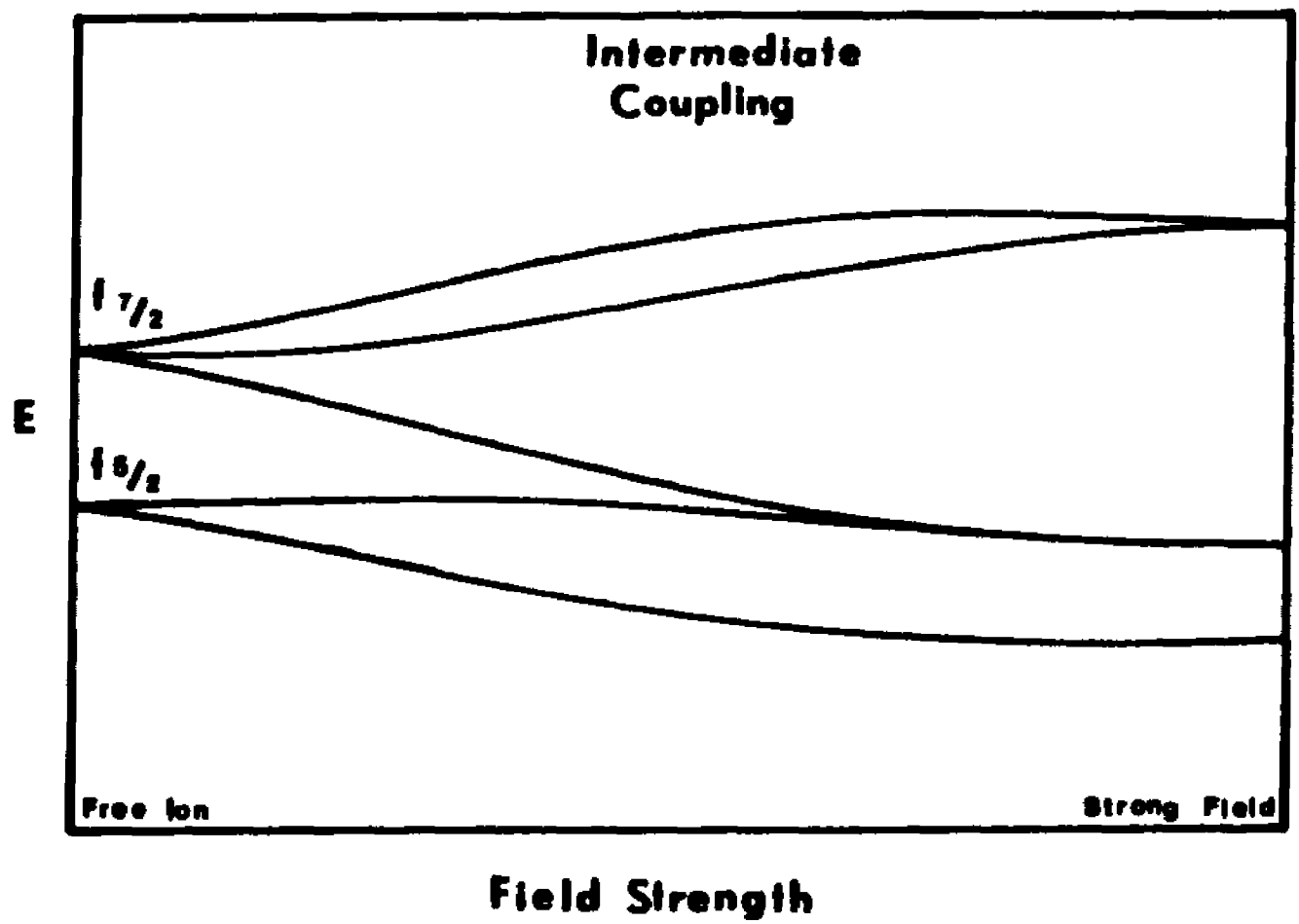

Γ_6
Γ_8'
Γ_7'
$J=7/2$
^2F
$L=3$
$S=1/2$
Γ_8
$J=5/2$
Γ_7

FIGURE XIX

Field Effects on the Energy Levels of a 5f Electron


Intermediate
Coupling
f 7/2
f 5/2
E
Free Ion
Strong Field
Field Strength

For the quadruply degenerate Γ_8 levels Jahn-Teller distortions will be significant. It is predicted that these levels will split into two levels when distortion of the octahedron occurs. On the basis of rough calculations Eisenstein and Pryce(123) expect the splitting to be of considerable magnitude. The Γ_8 levels may also interact with vibrational modes to produce weak, broad bands.

Vibrational selection rules indicate that the totally symmetric vibrational mode A_{1g} can couple with electronic transitions to produce bands of greatly diminished intensity.

It is predicted that the odd vibrational modes will couple most strongly with the electronic transitions.

For a 0-0 transition of frequency ν_0 and vibrational frequency ν, bands of frequency $(\nu_0 + \nu)$ and $(\nu_0 - \nu)$ are expected whose intensities are approximately in the ratio of $e^{h\nu/kT}:1$.

The theoretical model developed for the $5f^1$ system in an octahedral field cannot, of course, be used for a detailed interpretation of the spectra of these compounds because some of the important factors assumed for the calculations simply do not apply to these compounds. For example, the crystal field calculations exclude the possibility of covalent bonding. In these coordination compounds covalent bonding is, of course, very significant in the bonding of the compound. Furthermore, the symmetry of these new compounds is not the perfect octahedral symmetry assumed in the model. It is likely that the symmetry of $UCl_5 \cdot Ph_3P$ and $UCl_5 \cdot$diphos is close to C_{4v} and a lower symmetry is very probable for the other

compounds. Additionally, the model for the $5f^1$ system is based on a coordination number of six. Some of the new compounds appear to exhibit coordination number of six but others appear to show higher coordination numbers of seven, nine and possibly even ten. Despite these deviations from the conditions which were used to deduce the model for the $5f^1$ system it does seem possible to use some of the ideas of the model to understand the complex spectra obtained for these new compounds.

The electronic spectra are shown in Figures XX to XXIX and the absorption bands are given in Tables VIII and IX. The absorption bands have been assigned to the four predicted octahedral transitions: $\Gamma_7 \rightarrow \Gamma_8$, $\Gamma_7 \rightarrow \Gamma_7'$, $\Gamma_7 \rightarrow \Gamma_8'$, $\Gamma_7 \rightarrow \Gamma_6$. It is noted that very large numbers of bands occur for some transitions.

The spectra of $UCl_5 \cdot Ph_3P$, $(UCl_5 + Ph_3Sb)$, and $[U_2Cl_9(Ph_3Bi)]Cl$ are very similar. The spectrum of $UCl_5 \cdot$diphos exhibits considerably more splitting than the above compounds and the unsymmetrical complex $[U_2Cl_9(Ph_3As)]Cl$ shows even more splitting of the absorption bands.

The two compounds containing 8-hydroxyquinoline, $UCl_5 \cdot 2C_9H_7NO$ and $UCl_5 \cdot 4C_9H_7NO$ show less intense absorption than the other compounds. It has been found that $UCl_5 \cdot 4C_9H_7NO$ has an unusually high g_{ave}, 2.286, and a high magnetic moment, μ_{eff} = 2.48 BM. The unusual behavior of this compound is not clearly understood and further studies on it are surely in order.

FIGURE XX

Electronic Spectrum of $[UCl_4dipy]Cl$

in Nujol Mull at $77^{O}K$.

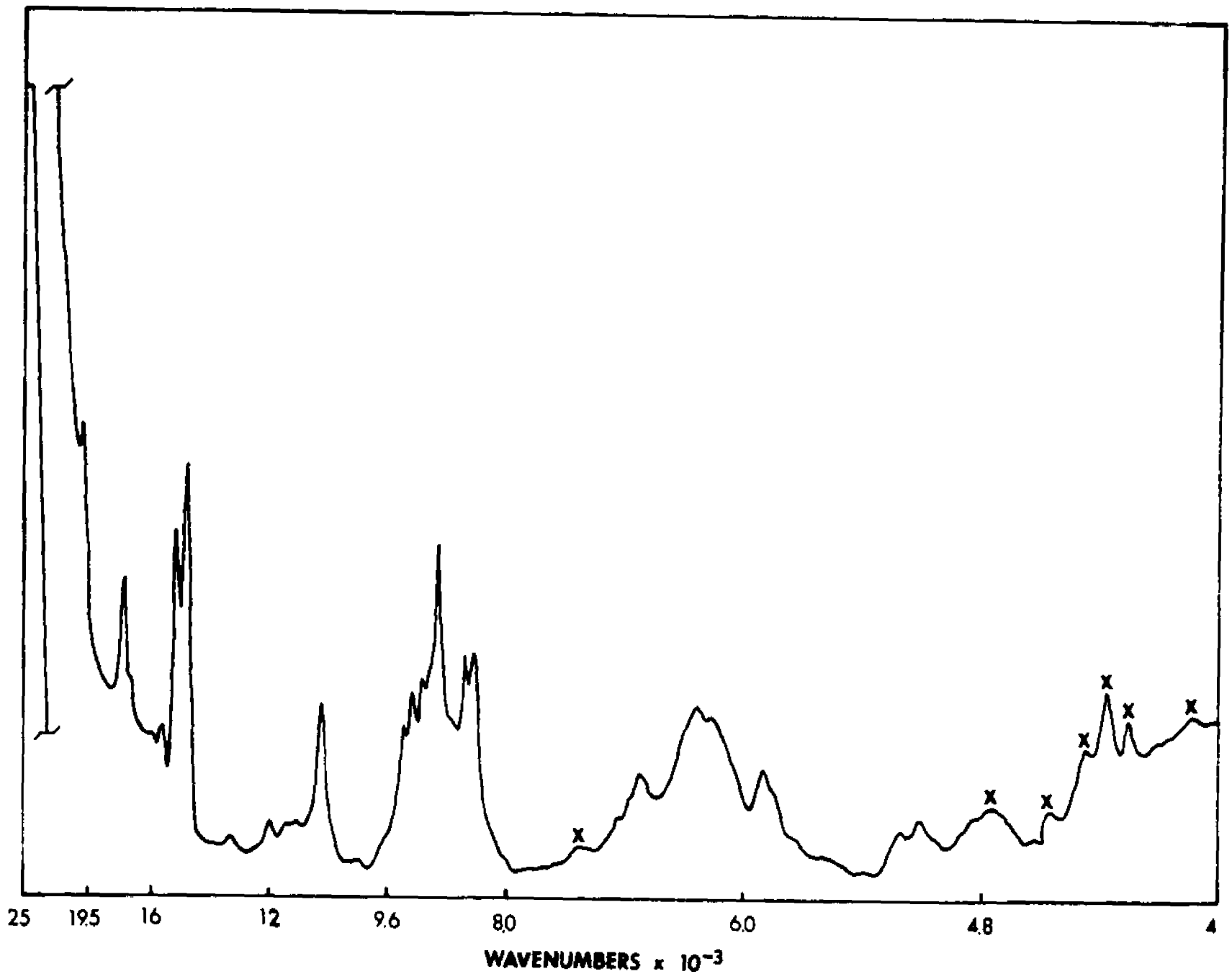

25
19.5
16
12
9.6
8.0
6.0
4.8
4
WAVENUMBERS x 10^{-3}

FIGURE XXI

Electronic Spectrum of $UCl_5 \cdot Ph_3P$ in

Nujol Mull at 77°K.

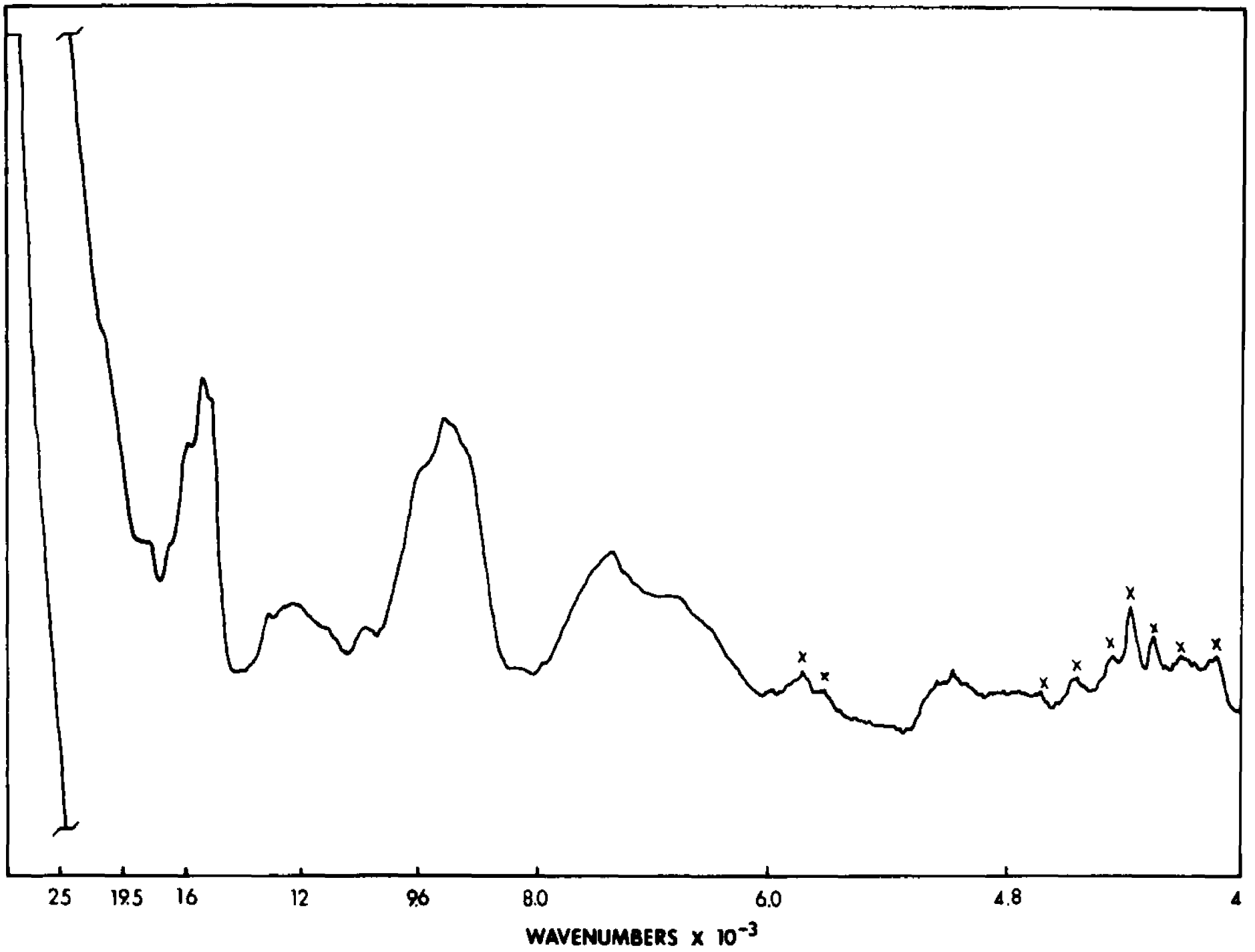

25
19.5
16
12
9.6
8.0
6.0
4.8
4
WAVENUMBERS x 10^{-3}

FIGURE XXII

Electronic Spectrum of UCl_5·diphos in Nujol Mull at 77°K.

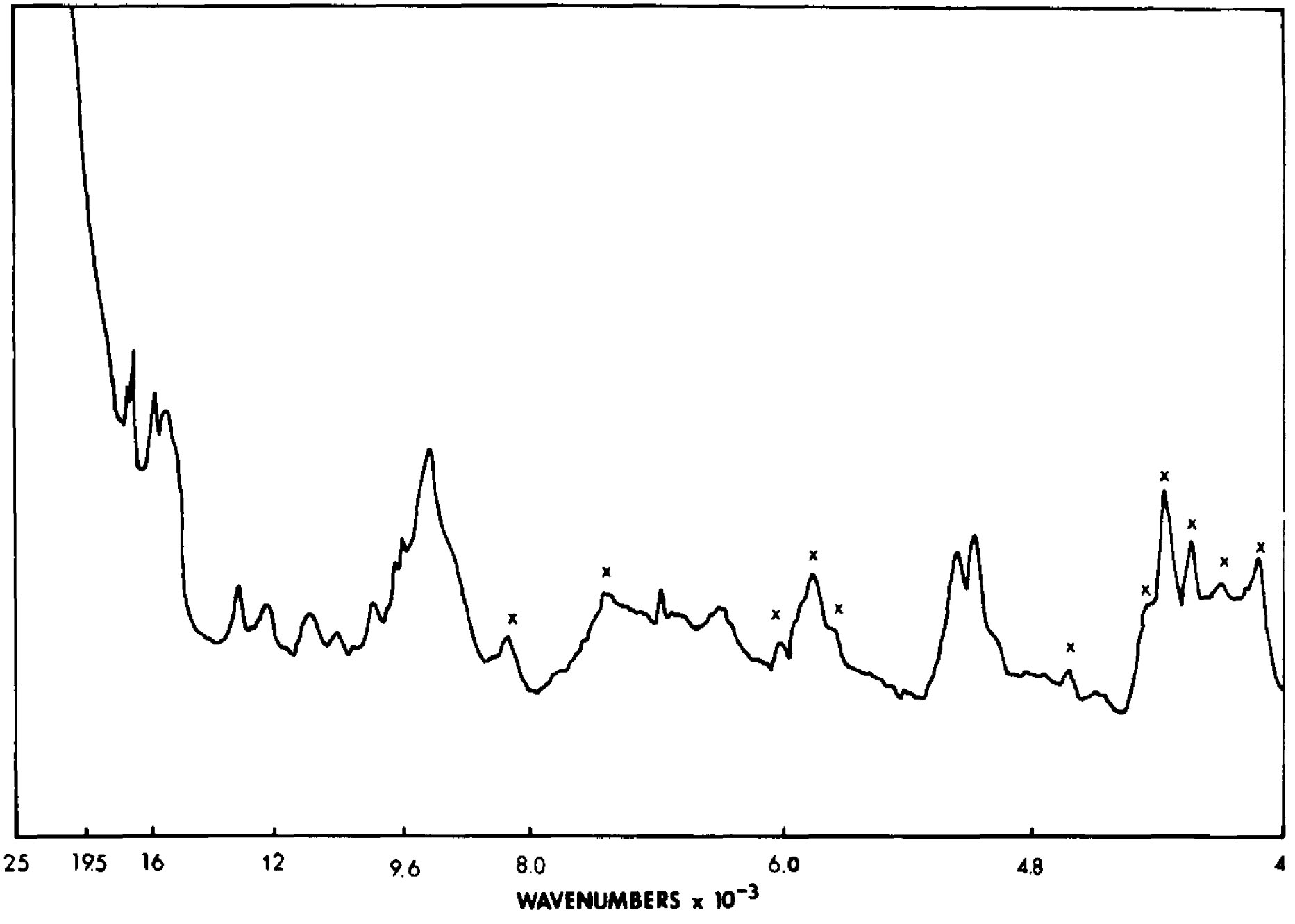

25
19.5
16
12
9.6
8.0
6.0
4.8
4
WAVENUMBERS x 10^{-3}

FIGURE XXIII

Electronic Spectrum of UCl_5·diphos in Nitromethane Solution at 298°K.

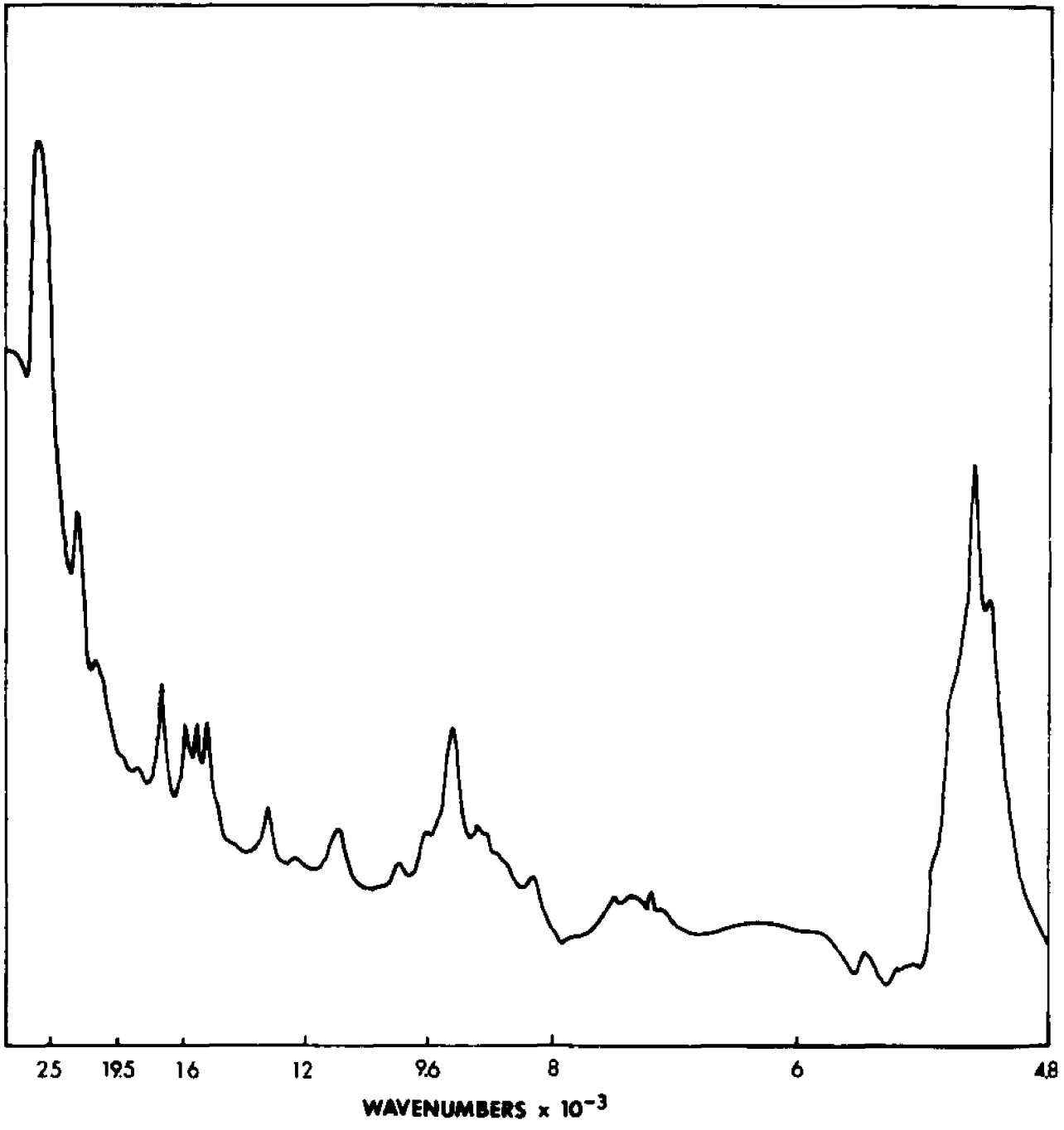

2.5
1.95
1.6
1.2
0.96
0.8
0.6
0.48
WAVENUMBERS x 10^{-3}

FIGURE XXIV

Electronic Spectrum of $[U_2Cl_9(Ph_3As)]Cl$ in Nujol Mull at 77° K.

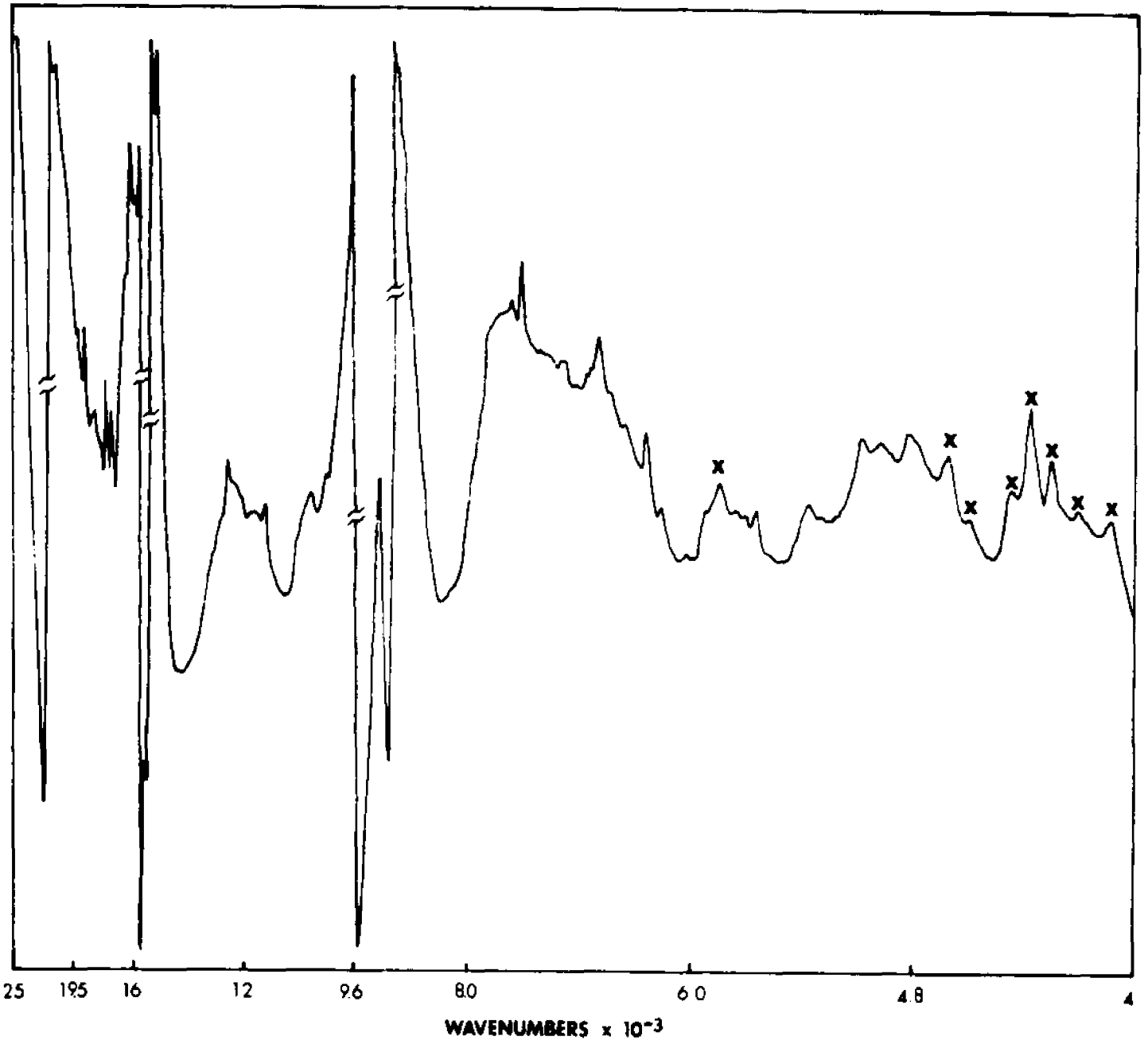

25
19.5
16
12
9.6
8.0
6.0
4.8
4
WAVENUMBERS x 10⁻³

FIGURE XXV

Electronic Spectrum of $[U_2Cl_9(Ph_3Bi)]Cl$

in Nujol Mull at $77^{O}K$.

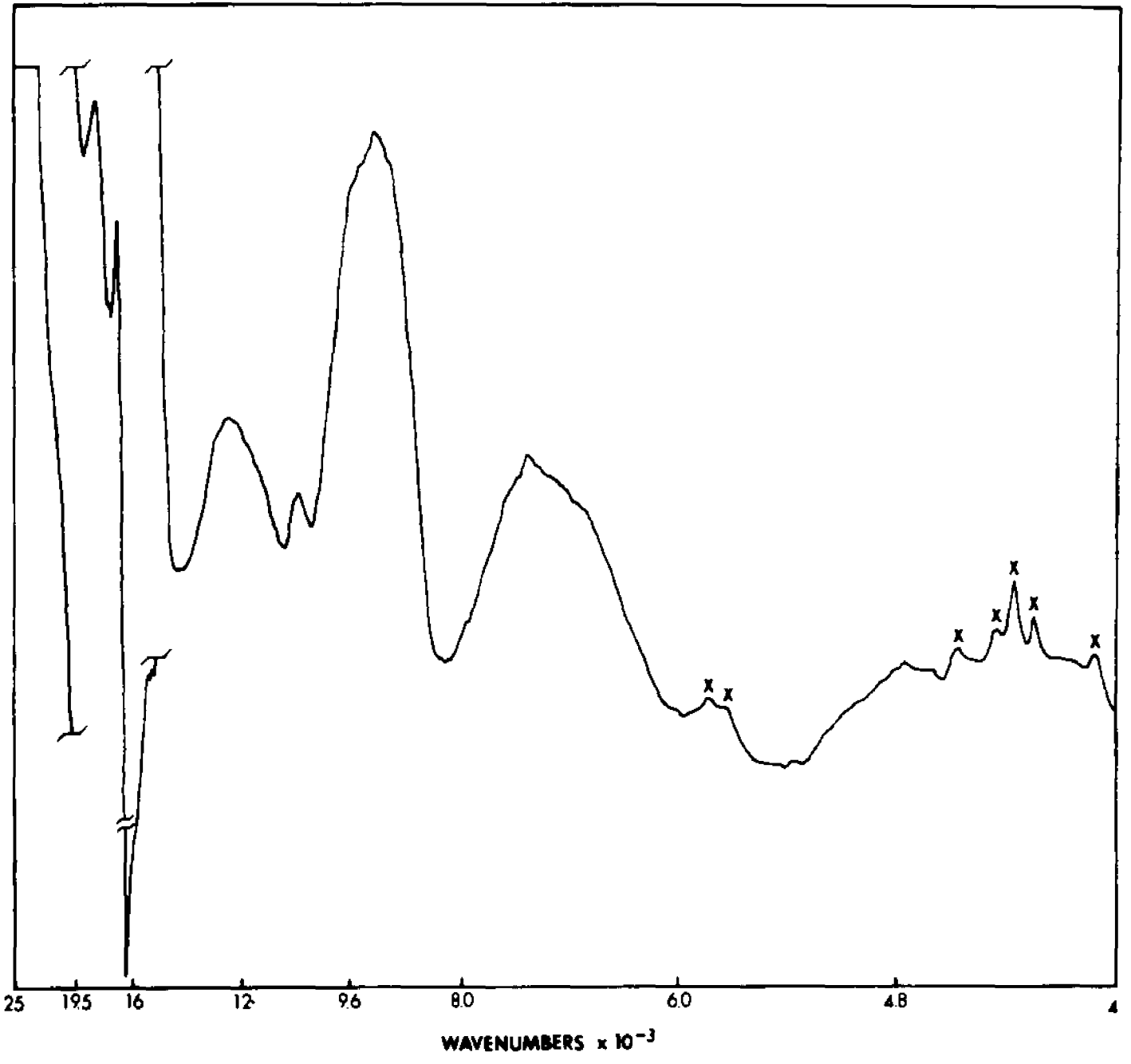

25
19.5
16
12
9.6
8.0
6.0
4.8
4
WAVENUMBERS x 10⁻³

FIGURE XXVI

Electronic Spectrum of $UCl_4T \cdot 4HT$ in

Nujol Mull at $77^{\circ}K$.

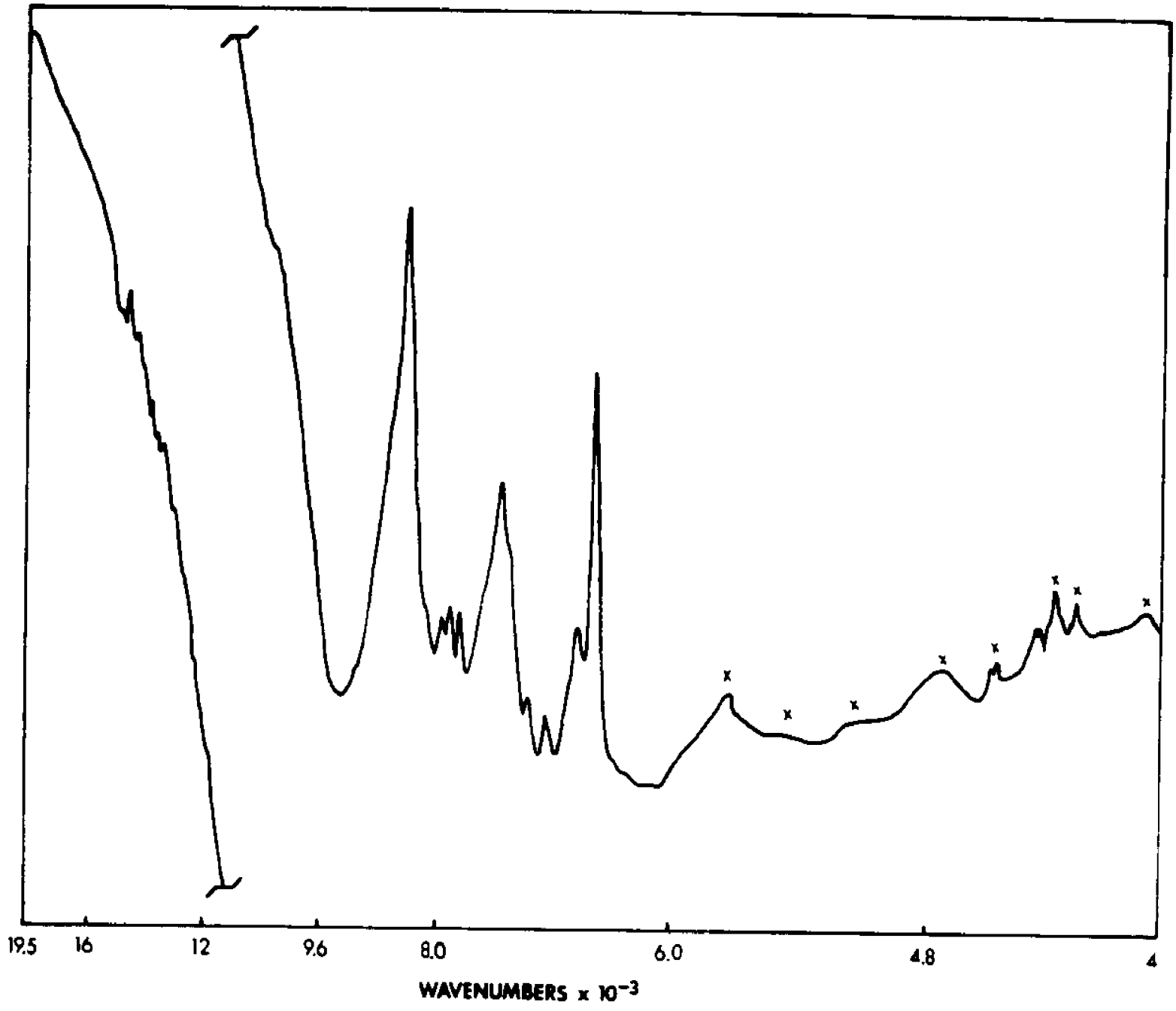

19.5
16
12
9.6
8.0
6.0
4.8
4
WAVENUMBERS x 10^{-3}

FIGURE XXVII

Electronic Spectrum of $UCl_5 \cdot 2C_9H_7NO$

in Nujol Mull at 77°K.

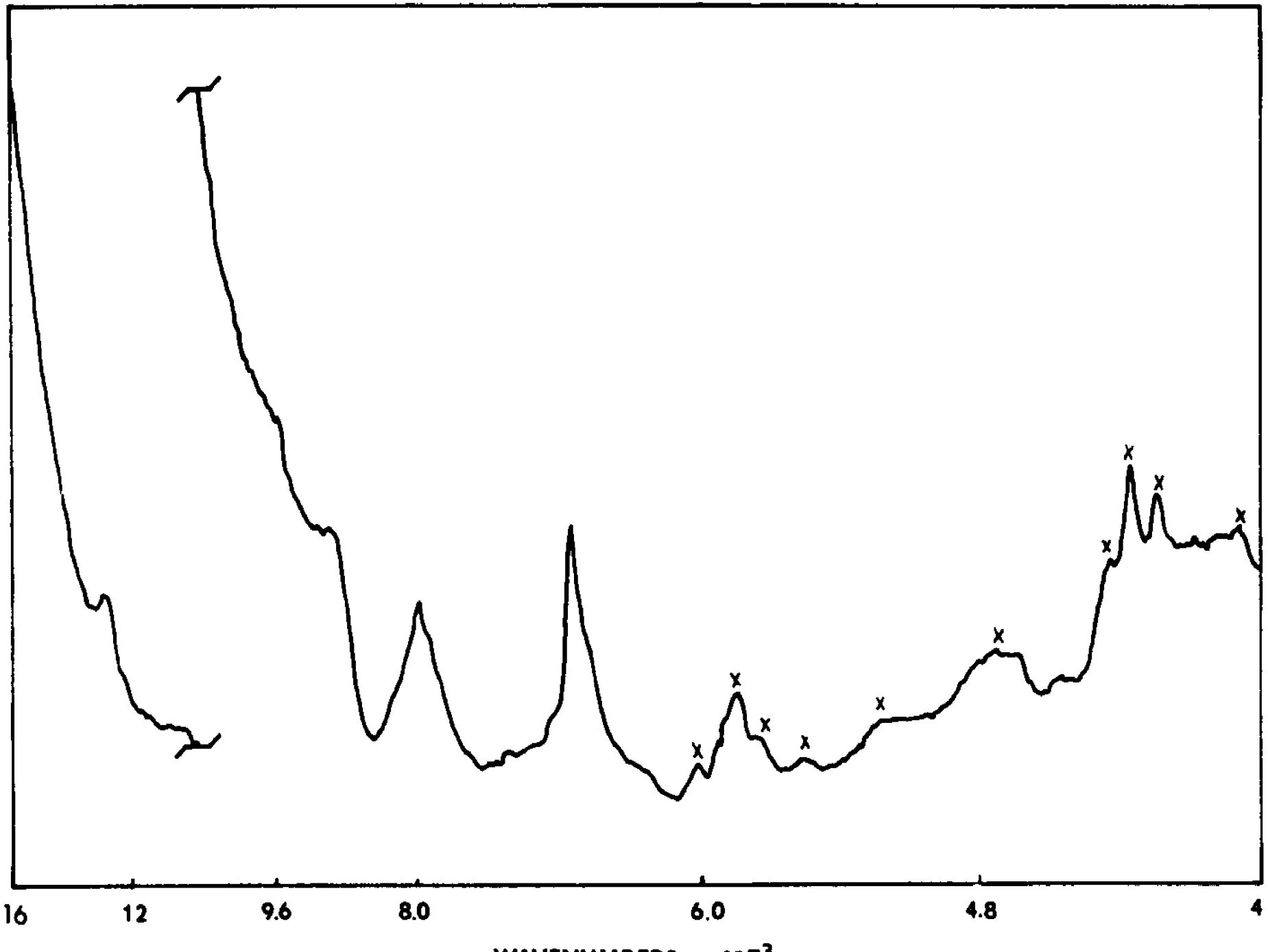

16
12
9.6
8.0
6.0
4.8
4

FIGURE XXVIII

Electronic Spectrum of $UCl_5 \cdot 4C_8H_7NO$ in Nujol Mull at $77^{\circ}K$.

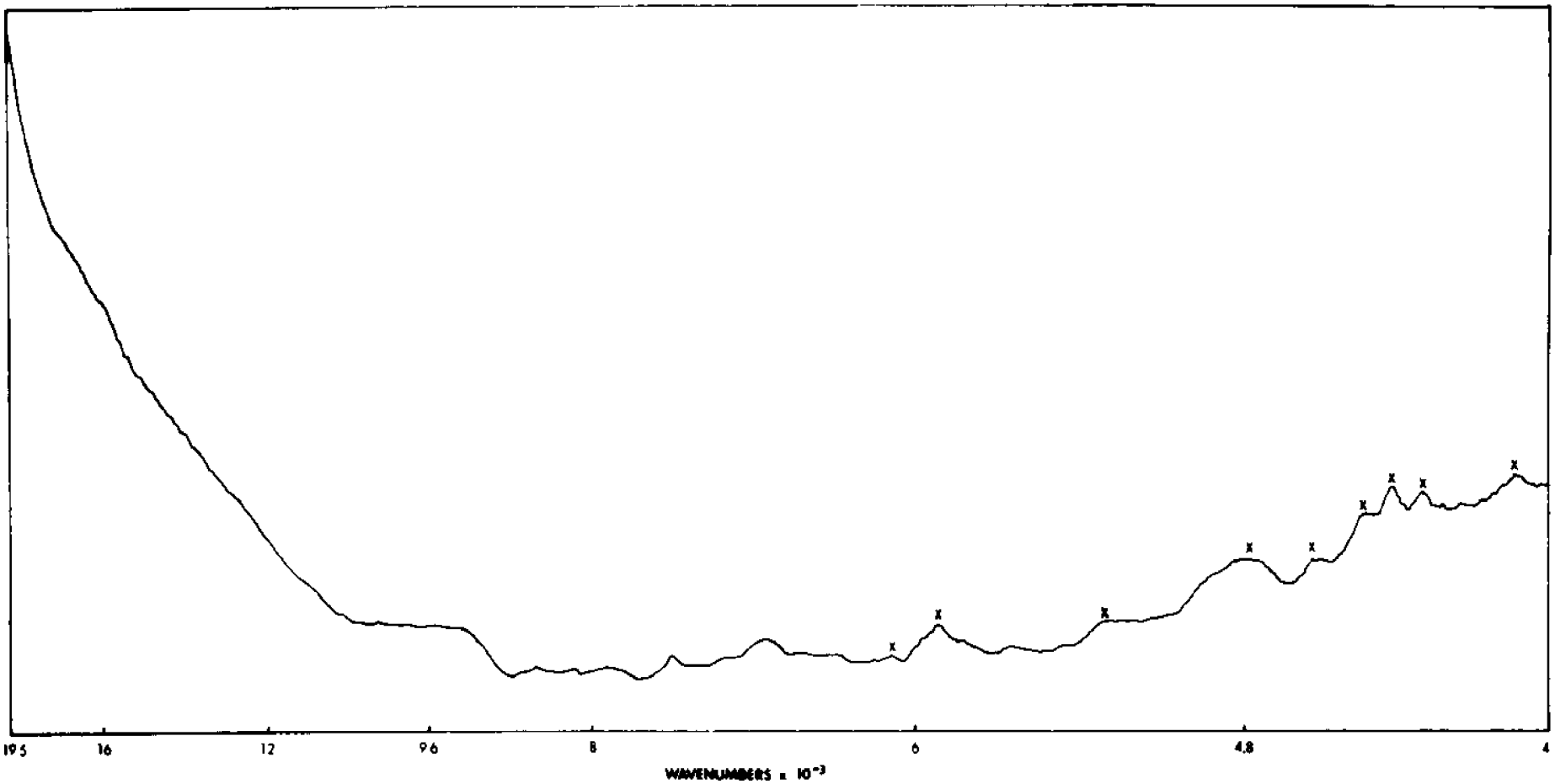

19.5
16
12
9.6
8
6
4.8
4
WAVENUMBERS x 10^{-3}

FIGURE XXIX

Electronic Spectrum of (UCl_5+Ph_3Sb)

in Nujol Mull at 77°K.

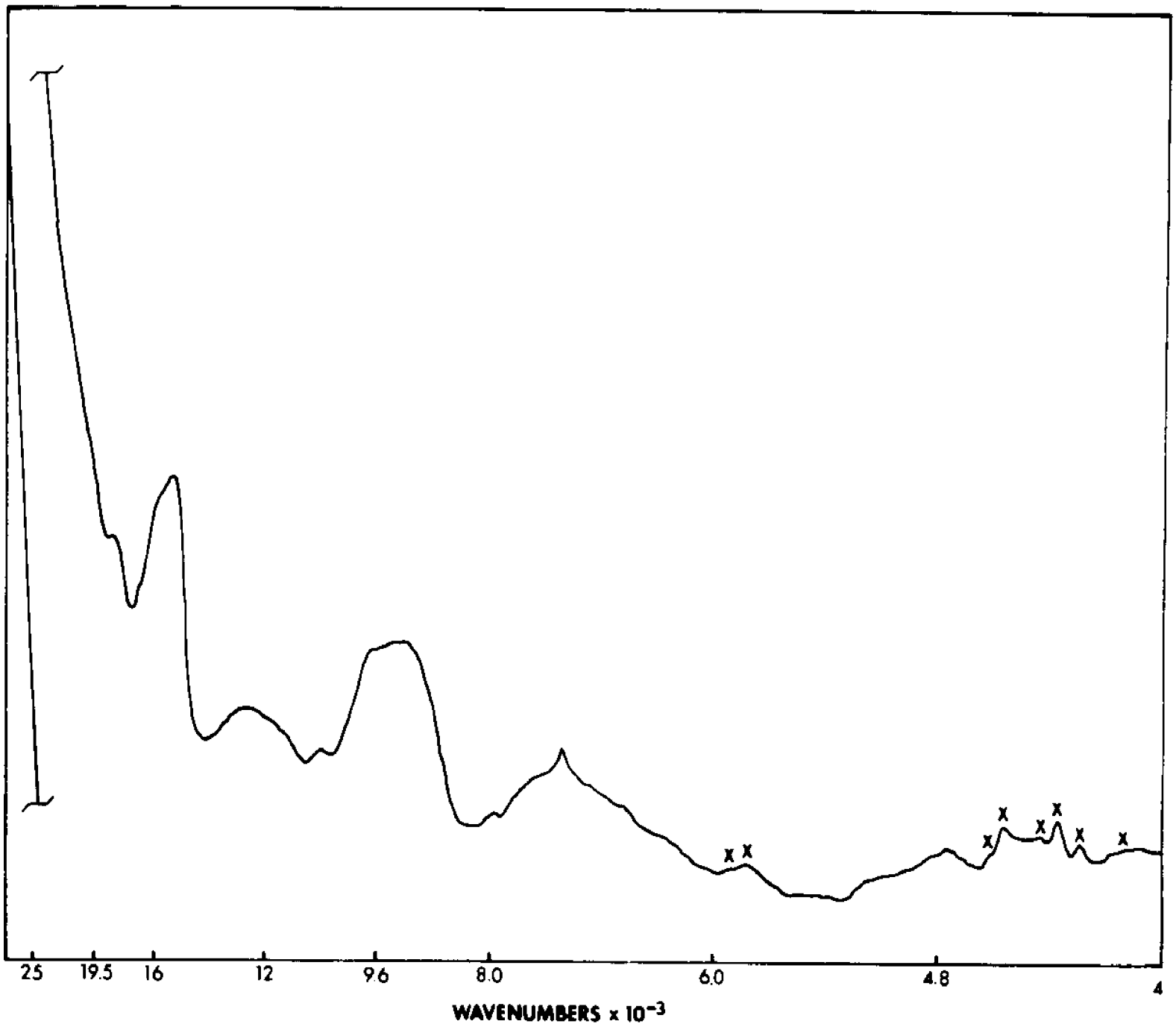

25
19.5
16
12
9.6
8.0
6.0
4.8
4
WAVENUMBERS x 10⁻³

TABLE VIII

VISIBLE AND NEAR-INFRARED ABSORPTION BANDS (cm^{-1}) OF URANIUM(V) COMPOUNDS WITH PHOSPHOROUS, ARSENIC, ANTIMONY AND BISMUTH DONOR LIGANDS[a]

$UCl_5 \cdot Ph_3P$	UCl_5·diphos	UCl_5·diphos[b]	$[U_2Cl_9(Ph_3As)]Cl$	UCl_5+Ph_3Sb	$[U_2Cl_9(Ph_3Bi)]Cl$	Assignments
40,316 L						
(35,714)						
33,058 s						
31,153 s						
(26,490)		25,807 s				
		22,422 s	23,175 s			
		22,149 m	(21,834)			
			(21,622)			
			(21,322)			
(20,838)		20,920 w	20,747 s			$\Gamma_7 \rightarrow \Gamma_8$
(19,960)		20,325 w	(20,492)			
(18,553)			20,040 s			
(17,922)			19,531 w			
(17,096)			(18,815)			
16,807 w			18,587 s	(18,450)		
(15,873)		18,182 w	18,215 w		18,149 s	
(15,241)			17,937 m			
(14,926)		(17,341)	(17,301)			
		16,964 s	17,036 s			
	16,992	(16,892)	(16,667)			
	16,864 m		16,129 s			
	16,751 s	15,927 m	(15,576)	(15,576)	(15,936)	
	(15,886)	15,798 w	(15,267)	15,198 s	15,267 s	
	15,736 m	(15,444)	15,244 s		(15,174)	
	(15,456)	15,349 s	(14,881)			
	15,314 m	(15,244)	14,837 s			

Table VIII cont.

$UCl_5 \cdot Ph_3P$	$UCl_5 \cdot diphos$	$UCl_5 \cdot diphos$[b]	$[U_2Cl_9(Ph_3As)]Cl$	$UCl_5 + Ph_3Sb$	$[U_2Cl_9(Ph_3Bi)]Cl$	Assignments
	15,174 m	15,186 m				
	(15,015)	15,015 s				
	14,925 w	14,916 m				
		14,802 w				
		14,663 w				
		13,952 m		(14,493)		
(12,937)	12,928 m			(13,518)		
12,225 m	12,194 m	12,195 w	(12,837)	12,739 m	12,446 m	
			(12,453)			
			12,210 s			
			(12,106)			
(11,442)	11,186 m	11,834 w	11,710 w			
		11,330 m	11,428 s			
10,554 m	10,706 w		(10,684)	10,753 w	10,712 m	
	10,030 m		(10,515)			
(9,524)			(10,438)			
9,200 s		10,153 w	10,373 s			
			(10,267)			
(9,066)		10,129 m	10,142 m			
(8,929)	(9,671)	9,709 m	(9,533)	(9,615)	(9,452)	
	9,574 m		(9,506)	9,259 s	9,238 s	$\Gamma_7 \rightarrow \Gamma_8'$
	(9,443)		9,363 s			
	9,174 s	9,281 s	9,187 s			
		8,879 m	9,107 s	(9,009)	(9,058)	
		(8,640)	(9,058)			
		(8,547)	8,993 s			
		8,163 m	(8,897)			
			8,803 s			
(8,177)	8,230 x					
7,273 s			(7,599)	(7,936)	(7,968)	
(6,644)			(7,463)	(7,299)	(7,380)	

Table VIII cont.

$UCl_5 \cdot Ph_3P$	UCl_5·diphos	UCl_5·diphos[b]	$[U_2Cl_9(Ph_3As)]Cl$	UCl_5+Ph_3Sb	$[U_2Cl_9(Ph_3Bi)]Cl$	Assignments
		7,408 m	7,364 m			
	7,225 x	7,248 m	7,225 x	7,210 m	7,260 m	
	6,798 m	7,080 s	6,963 m	(7,018)	(7,231)	$\Gamma_7 \rightarrow \Gamma_7'$
	6,365 w	6,986 w	6,656 s	(6,644)		
			6,289 s	(6,369)	(6,031)	
			6,177 m	(6,250)		
			6,010 w			
			5,797 x			
	6,010 x					
			5,626 m	5,907 x	5,797 x	
6,006 x	(5,893)		5,590 m	5,780 x	5,701 x	
5,797 x	(5,862)		5,574 m	(5,155)	(5,256)	
5,682 x	5,797 x		5,277 w	4,762 w	(4,878)	
	5,685 x	5,088 w	5,025 s	(4,693)	4,760 w	
5,089 w	5,093 s	5,032 s	4,796 m	4,574 x	4,651 w	
5,020 m	5,018 s		4,630 s	4,535 x	4,543 x	
	(4,949)		4,540 x	4,405 x	4,398 x	
	4,768 x		4,400 x	4,334 x	4,342 x	$\Gamma_7 \rightarrow \Gamma_8$
	4,563 w		4,329 x	4,264 x	4,260 x	
	4,393 x		4,253 x	4,065 x	4,072 x	
	4,331 x		4,065 x			
	4,258 x					
	4,168 x					
	4,064 x					

[a] Bands marked with an x are due to ligand or Nujol absorption.

[b] Data for a room temperature spectrum of a nitromethane solution of UCl_5·diphos. All other data are from spectra obtained at 77°K using Nujol mulls of the compounds.

TABLE IX

VISIBLE AND NEAR-INFRARED ABSORPTION BANDS (cm^{-1}) OF URANIUM(V) COMPOUNDS WITH OXYGEN AND NITROGEN DONOR LIGANDS[a]

$UCl_4T.4HT$	$UCl_5 \cdot 2C_9H_7NO$	$UCl_5 \cdot 4C_9H_7NO$	$[UCl_4dipy]Cl$	Assignments
(14,409)				
(13,889)			19,512 s	
(13,423)			(19,379)	
(13,333)		Bands	(17,241)	
(13,140)		covered	17,021 s	
(12,820)		by	16,750 m	$\Gamma_7 \rightarrow \Gamma_6$
(12,563)		intense	15,748 w	
(12,048)	(12,598)	absorption	15,326 m	
(11,834)			14,793 s	
(10,348)			14,388 s	
		(9,896)		
			12,987 w	
			11,905 m	
	(8,913)		11,494 w	
(9,070)		(8,909)	11,236 w	$\Gamma_7 \rightarrow \Gamma_8'$
8,333 s			10,707 s	
(8,097)			(10,428)	
			(10,309)	
			10,005 w	
(7,981)			(9,569)	
7,936 m			9,302 m	
7,831 m			9,141 s	
7,737 m			9,001 s	
			8,791 s	
(7,468)			8,602 m	$\Gamma_7 \rightarrow \Gamma_7'$
7,326 s			8,439 s	
(7,246)	7,971 s		8,326 s	
7,060 m			(8,114)	
6,944 m		7,936 x	7,936 w	
	7,225 x	7,225 x	7,225 x	
(6,711)	(6,896)		6,897 w	
6,644 m			6,803 m	
6,536 s	6,754 s	6,667 x	6,711 s	
(6,369)			(6,382)	
(6,281)	6,002 x	6,006 x	6,278 s	$\Gamma_7 \rightarrow \Gamma_8$
	5,805 x	5,797 x	6,173 s	
5,974 x	5,674 x	5,695 x	(6,042)	
5,284 x	5,155 x	5,161 x	5,865 m	

Table IX cont.

$UCl_4T \cdot 4HT$	$UCl_5 \cdot 2C_9H_7NO$	$UCl_5 \cdot 4C_9H_7NO$	$[UCl_4dipy]Cl$	Assignments
4,762 x	4,891 x	(4,981)	(5,780)	
4, 545 x	4,755 x	4,739 x	5,038 m	
4,400 w	4,624 x	(4,686)		
4,237 x	4,400 x	4,440 x	4,750 x	$\Gamma_7 \rightarrow \Gamma_8$
4,264 x	4,331 x	4,331 x	4,515 x	
4,057 x	4,260 x	4,260 x	4,396 x	
		4,065 x	4,338 x	
			4,255 x	
			4,026 x	

[a]Bands marked with an x are due to ligand or Nujol absorption.

The tropolone complex, assumed to be ten coordinate, shows a spectrum somewhat different from the other compounds. A distinct difference is noted in the intensity, shape and splitting of the absorption band for the $\Gamma_7 \rightarrow \Gamma_8$ transition. The other bands also show differences when compared to the other compounds.

Comparing the compounds containing oxygen and nitrogen donor atoms with the compounds containing phosphorous, arsenic, antimony and bismuth donors atoms it is noted that the $\Gamma_7 \rightarrow \Gamma_8$ transition occurs at ~ 1000 cm^{-1} higher energy for the oxygen and nitrogen donor compounds. The other transitions are also found at higher energies for the oxygen and nitrogen donor compounds. These differences undoubtedly reflect the differences in ligand field strength of the various donor atoms.

Using the Jorgensen idea of average ligand field strength, it is of interest to try to arrange the ligands in a spectrochemical series. The calculations are based on the O→O transition for the $\Gamma_7 \rightarrow \Gamma_7'$ transition which is predicted to be stabilized by spin orbit coupling and is not expected to be affected by Jahn-Teller distortions. The value for UCl_6^- will be used as the reference point and the calculations made in the following way with X representing any ligand other than Cl^-.

$$E_{UCl_5X} = \frac{1}{6}E_{UX_6} + \frac{5}{6}E_{UCl_6^-}$$

$$E_{UX_6} = 6[E_{UCl_5X} - \frac{5}{6}E_{UCl_6^-}]$$

Calculations were made for the six-coordinate compounds prepared in this study and for some compounds prepared by other workers. The results of the calculations are given in Table X. The energy values

TABLE X

OBSERVED AND CALCULATED VALUES FOR $\Gamma_7 \rightarrow \Gamma_7'$ TRANSITIONS FOR URANIUM(V) COMPOUNDS

Actual Compound	Observed $\Gamma_7 \rightarrow \Gamma_7'$ (cm^{-1})	Hypothetical Compound	Calculated $\Gamma_7 \rightarrow \Gamma_7'$ (cm^{-1})
UCl_6^{-a}	6798		
UF_6^{-a}	7407		
UBr_6^{-a}	6817		
$UCl_5 \cdot TCAC$	6873	$U(TCAC)_6$	7,236
$[UCl_4dipy]Cl$	8791	$U(dipy)_3$	12,777
$UCl_5 \cdot Ph_3P$	7273	$U(Ph_3P)_6$	9,647
$UCl_5 \cdot diphos$	6798	$U(diphos)_6$	6,798

[a]The data for these compounds is from unpublished work by Jack L. Ryan.

for the 0–0 transitions in the $\Gamma_7 \rightarrow \Gamma_7'$ transition are from solid state spectra in all cases.

The following "spectrochemical series" is obtained:

$$\text{dipy} > F^- > Ph_3P > \text{TCAC} > Br^- > Cl^- = \text{diphos}$$

The position of Ph_3P seems anomalous while that for diphos seems more reasonable for a phosphorous donor ligand. The absorption band for the 0–0 transition for the $\Gamma_7 \rightarrow \Gamma_7'$ transition is rather broad and it may be that the value used in the calculation is not the proper value. The energy used in the calculation is that for the sharpest and most intense band of the broad absorption envelope.

It is seen that the relative positions of F^- and Cl^- are as would be expected. Br^- appears as a slightly stronger ligand than Cl^- which is contrary to what is usually observed. The difference between Br^- and Cl^- is however, very small, 19 cm^{-1}. The relative position of dipy and TCAC are as might be expected for oxygen and nitrogen donors.

It is predicted from theory that the quadruply degenerate Γ_8 levels will be split into two levels when distortion of the octahedron occurs. This splitting is observed for most of the compounds along with additional splitting presumably the result of interaction with vibrational modes.

E. Mass Spectra

The mass spectra were obtained for $UCl_4T \cdot 4HT$, $UCl_5 \cdot Ph_3P$, $[U_2Cl_9(Ph_3As)]Cl$ and $UCl_5 \cdot 4C_9H_7NO$. The data for these spectra are given in Table XI.

TABLE XI

DATA FOR MASS SPECTRA

$UCl_4T \cdot 4HT$

Temperature, °C	Mass, AMU	Relative Intensity	Fragment
250°	207	w	?
90°-250°	122	s	HT
90°-250°	94	s	C_6H_6O
90°-250°	78	s	C_6H_6

$UCl_5 \cdot Ph_3P$

Temperature, °C	Mass, AMU	Relative Intensity	Fragment
150°	368	w	$(Ph_2P)_2$
125°-200°	277	m	?
125°-200°	262	s	Ph_3P
150°-200°	185	w	Ph_2P^+
150°-200°	183	s	
200°	109	m	
200°	108	s	Ph-P
200°	107	m	?
75°	77	s	Ph-

$[U_2Cl_9Ph_3As]Cl$

Temperature, °C	Mass, AMU	Relative Intensity	Fragment
250°	395	w	?
215°-250°	306	s	Ph_2As
155°-250°	264	w	?
175°-250°	229	w	Ph_2As^+
175°-250°	227	w	
175°-250°	187	s	$As-C_6H_4Cl$
105°-250°	154	s	Ph-Ph
105°-250°	152	s	Ph-As
175°-250°	112	s	Ph-Cl
155°-250°	77	s	Ph-

$UCl_5 \cdot 4C_9H_7NO$

Temperature, °C	Mass, AMU	Relative Intensity	Fragment
205°	422	vw	?
205°	394	vw	?
205°	368	vw	?
55° -205°	145	s	C_9H_7NO
55° -205°	117	s	C_9H_7N
160° -205°	90	m	C_7H_8
160° -205°	89	m	C_7H_5
160° -205°	63	m	?

In the spectrum of $UCl_4T \cdot 4HT$ a peak corresponding to the mass of the ligand, HT, is present. Tropolone yields the phenol ion, $C_7H_5OH^+$, as a result of elimination of carbon monoxide(126) and this fragment has a mass of 94. A strong peak with a mass of 78 is not found in the mass spectrum of tropolone. However, tropone, C_8H_8O, does fragment by eliminating CO and yielding the benzene ion-radical. (126) The presence of a fragment of mass 78 in the spectrum of $UCl_4T \cdot 4HT$ may indicate that as a result of coordination to uranium, tropolone leaves an oxygen attached to the uranium and then fragments as does tropone.

The spectra for $UCl_5 \cdot Ph_3P$ shows fragments corresponding to the mass of the ligand, Ph_3P, PhP- and Ph-. The investigation of the mass spectrum of Ph_3P(126) has shown that its most important fragment has a mass of 183 and this originates from the decomposition of $(C_8H_5)_2P^+$, mass 185, by loss of H_2 to yield  . The mass spectrum of $UCl_5 \cdot Ph_3P$ shows fragments of mass 185 and 183. The fragment with mass 368 is thought to be $(Ph_2P)_2$. It is significant that no peak corresponding to $Ph_3P = O$ is observed. This is additional evidence that the compound prepared in this study does not contain triphenylphosphine oxide.

In the spectra of $[U_2Cl_9(Ph_3As)]Cl$ masses corresponding to the ligand, Ph_3As, and fragments Ph-Ph, Ph-As and Ph- are present. It is assumed that triphenylarsine would fragment in a pattern similar to that observed for triphenylphosphine. The fragments with mass 229 and 227 could then be considered due to $(C_8H_5)_2As^+$ and  .

Other peaks present in the spectrum of the complex are thought to be due to Ph-Cl and As-C_6H_4Cl. It can be noted that a mass corresponding to $Ph_3As{=}O$ is not present. This confirms that the compound does not contain triphenylarsine oxide.

A strong peak corresponding to the mass of the ligand is found in the spectrum of $UCl_5 \cdot 4C_9H_7NO$. The hydroxyquinolines fragment (126) by losing CO to give a fragment of mass 117. This is followed by expulsion of HCN with and without an additional hydrogen to give fragments of mass 90 and 89. Fragments with masses of 117, 90 and 89 are observed in the mass spectrum of $UCl_5 \cdot 4C_9H_7NO$.

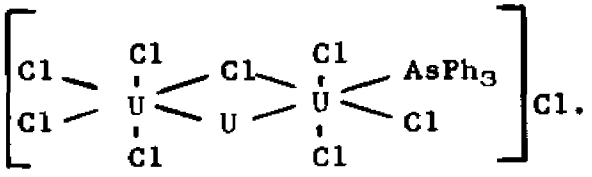
F. Conclusions

This study has resulted in the preparation of the first well characterized uranium(V) complex with a nitrogen donor ligand. This ionic compound, $[UCl_4dipy]Cl$, is extremely unstable. The oxidation state of uranium has been verified by ESR, determination of magnetic moment and the electronic spectrum. The assignment of the frequencies of the U-Cl and U-N bonds have been made.

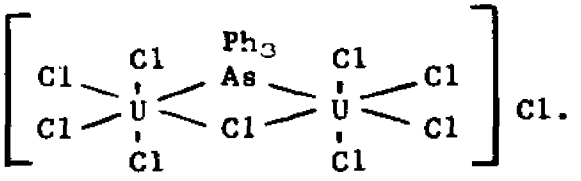
The two compounds with phosphorous donor ligands are the first uranium(V) compounds containing the U-P band. The ESR data, the magnetic moment and the electronic spectra confirm the presence of uranium(V) in these compounds. The frequencies for the U-P band have been assigned along with the U-Cl frequencies in these compounds.

$[U_2Cl_9(Ph_3As)]Cl$ is a new type of uranium(V) compound. The presence of uranium(V) is confirmed by the magnetic moment and electronic spectrum. It appears that in the formation of $[U_2Cl_9(Ph_3As)]Cl$

the dimeric structure of uranium pentachloride is not cleaved but that the Ph_3As simply replaces one terminal chlorine in $(UCl_5)_2$. The presence of a fragment in the mass spectrum with a mass of 112 corresponding to Ph-Cl would appear to support the presence of one ionic chloride in the compound. It is noted that no fragment with a mass of 112 corresponding to Ph-Cl is present in mass spectrum of $UCl_5 \cdot Ph_3P$ which does not contain an ionic chloride. It appears that the arsenic donor complex is best represented by the formula



A structure containing chlorine bridging is supported by the fact that the compound does not give an ESR signal. If the two uranium atoms in the molecule are close enough to interact the ESR signal may be quenched. The fact that the magnetic moment per uranium atom in this compound is somewhat lower than is obtained for the other compounds also suggests interaction of the electrons of the two uranium atoms. An alternative structure might involve the Ph_3As in the bridging between the two uranium atoms to produce the symmetrical structure



However, this structure would assume that the lone pair of electrons on the arsenic atom has split and that an electron then pairs with

the single 5f electron on each of the two uranium atoms. The unsymmetrical structure with chlorine bridging seems preferable. There is evidence to suggest that the compound $[U_2Cl_9(Ph_3Bi)]Cl$ has a structure like that suggested for $[U_2Cl_9(Ph_3As)]Cl$. However, $[U_2Cl_9(Ph_3Bi)]Cl$ gives an ESR signal. This difference in behavior of the two compounds cannot be explained at present. However, the latter compound may have some monomer present which, even in small amount, would yield an ESR signal.

The stability of $UCl_4T\cdot 4HT$ makes this compound unique among the compounds prepared. This compound is apparently ten-coordinate, with the tropolonate anion acting as a bidentate ligand and the four tropolone molecules bonded as monodentate ligands. A ten coordinate compound of uranium(IV) has previously been prepared and studied. (82, 127) $LiUT_5$ (a uranium(IV) compound) has been shown to be ten coordinate. The presence of uranium(V) in $UCl_4T\cdot 4HT$ has been confirmed in this compound by ESR, magnetic moment and electronic spectrum.

The two compounds containing 8-hydroxyquinoline, $UCl_5\cdot 2C_9H_7NO$ and $UCl_5\cdot 4C_9H_7NO$, are extremely unstable. The magnetic moments, ESR and electronic spectra verify that these compounds contain uranium(V). $UCl_5\cdot 2C_9H_7NO$ is possibly a nine coordinate compound. It is not clear from the evidence which has been obtained what the coordination number would be in $UCl_5\cdot 4C_9H_7NO$. It may also be a ten coordinate compound. The U-N and U-O frequencies have been assigned in $UCl_5\cdot 4C_9H_7NO$.

The electronic spectra of these new uranium(V) compounds are quite complex. The four groups of bands corresponding to the four predicted transitions for a $5f^1$ system have been assigned for all the new compounds.

G. Suggestions for Future Work

In view of the preparation of $[U_2Cl_9(Ph_3Bi)]Cl$ it seems that additional work should be done in an attempt to obtain a pure compound with Ph_3Sb as the ligand. Work was stopped with this ligand because it appeared that the reaction of Ph_3Sb and UCl_5·TCAC was incomplete. However, since the compounds containing arsenic and bismuth have been established it seems likely that the antimony compound can be made.

The reaction of UCl_5·TCAC and ethylenebisdiphenylarsine yielded an impure compound which was quite similar in appearance to the $[U_2Cl_9(Ph_3As)]Cl$. An additional attempt to prepare this compound with some modifications of procedure based on the experience with reaction involving triphenylarsine may yield a pure compound.

The unusual stability of UCl_4T·4HT indicates that further work with the tropolone ligand would be of interest. UCl_4T·4HT, presumed to be a ten coordinate compound contains tropolone radical and molecular tropolone. It may be possible to vary the number of tropolone molecules which will bond to the UCl_4T group by varying the molar ratio of the reactants. A longer reaction time for UCl_5·TCAC and tropolone might result in substitution of more than one Cl^- in UCl_5. It would be of interest to determine whether compounds with

the tropolone ligand but with lower coordination number would prove to be as stable as $UCl_4T \cdot 4HT$.

The successful preparation of the compounds in this study by the reaction of UCl_5·TCAC with various ligands indicates that a variety of other ligands would yield compounds of interest.

The use of solvents other than benzene in the preparation of uranium(V) complexes should be explored. Although it was found that the use of toluene in the preparation of $[U_2Cl_9(Ph_3As)]Cl$ did not offer any advantage over benzene other reactions might be favorably affected by a different solvent.

The use of compounds other than UCl_5·TCAC should be used as the source of uranium(V) for the preparation of uranium(V) complexes. Compounds containing the UF_6^-, UCl_6^- and UBr_6^- may be useful as starting materials. Some of the compounds prepared in this study might also be useful in the preparation of other new compounds.

The results of electron spin resonance studies indicate that a more detailed study in this area should yield more information concerning the structure of these uranium(V) compounds. Additional work with solutions of these compounds should provide interesting ESR information.

It is hoped that when additional theoretical calculations are made for the $5f^1$ system that a more detailed interpretation of the electronic spectra of these compounds will be possible.

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VITA

Mary Jo Pribble is a native of Macfarlan, West Virginia where she received her elementary education. She was graduated from Harrisville High School in Harrisville, West Virginia. She received a Bachelor of Arts degree from Maryville College, Maryville, Tennessee in 1952. Following three years employment she entered graduate school at Duke University, Durham, North Carolina where she received her Master of Arts degree in 1957. She joined the faculty of Marietta College, Marietta, Ohio where she was Instructor of Chemistry for two years. From 1959 to 1961 she was employed as a Documentation Chemist in the Research and Development Section of the Ethyl Corporation, Baton Rouge, Louisiana. Returning to her native State she was Instructor of Chemistry at Marshall University, Huntington, West Virginia for two years. She was a National Science Foundation Research Participant at the University of Tennessee, Knoxville, Tennessee during the summers of 1962 and 1963. She went to Limestone College, Gaffney, South Carolina in 1963 as Assistant Professor of Chemistry and was promoted to Associate Professor of Chemistry in 1967.

During the summers of 1964 and 1965 Miss Pribble did graduate study at Louisiana State University as a National Science Foundation Institute Participant. She continued graduate study during the summers of 1966 and 1967. Since June, 1968 she has been

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EXAMINATION AND THESIS REPORT

Candidate: Mary Jo Pribble

Major Field: Chemistry

Title of Thesis: New Coordination Compounds of Uranium(V)

Approved:

Joel Selbin
Major Professor and Chairman

Max Gardner
Dean of the Graduate School

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Date of Examination:

August 6, 1969